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The Raman Effect in Crystal Powders of Inorganic Nitrates

By

P. KRISHNAMURTI

(Plate I)

(*Received for publication, 14th March, 1930*)

ABSTRACT

Raman spectra of nineteen inorganic nitrates in the form of small crystals or crystalline lumps have been obtained with improved technique. The inactive frequency of the NO_3 ion appeared prominently in all cases as a sharp line, but its position varied slightly from substance to substance. The greatest departure from its value in solution (1050^{-1} cm.) was observed with the light metals on the one hand (Li, Na and Mg) and with heavy metals on the other (Hg, Bi and Th). The isotropic crystals of barium and lead nitrates gave normal values, and it is concluded that the influence of the metal ion on the inactive frequency depends primarily on the volume occupied by the metal ion in the crystal lattice. In some cases (*e.g.*, Li, Hg (ic) and Al nitrates) the line was accompanied by a fainter component attributable to a polymerised molecule.

In several nitrates a line at about 7 μ appeared, sharp in a few cases (Li and Na) and diffuse in others. A sharp line at about 14 μ was also observed in many cases. These two correspond roughly to two of the infra-red frequencies of the nitrates observed by Schaefer and Schubert. The lattice frequencies appeared prominently only with Li and Hg (ous) nitrates and faintly with Na and Pb nitrates. A concentrated solution of lithium nitrate, however, failed to show this line as is to be expected if it corresponds to a characteristic lattice oscillation.

Introduction.

The recent experiments of Dr. A. C. Menzies[1] and of Prof. Bar of Zurich,[2] substituting powdered crystals for the not-readily-accessible single crystals in the study of the Raman spectra, have opened up a wide field for research. Both Bar and Menzies found some difficulty on account of the continuous spectrum produced by reflection from the crystals, which was sufficient to mask all but the strongest Raman lines. Several attempts were made by the present author to get rid of this continuous spectrum in the neighbourhood of the 4358 group of lines of the mercury arc where it is most intense, without however reducing the intensity of the lines themselves. An efficient filter of this type was found in a concentrated aqueous solution of didymium chloride, which served to bring out the fainter Raman lines with short exposures. The experimental arrangements used were slightly different from those used by Prof. Bar. The crystalline inorganic nitrates were first examined because a large number of them were easily available, thus enabling a study of the changes in the Raman lines with changes in the metallic constituents. An iron arc spectrum was photographed on each plate, and hence an accurate comparison of the Raman spectra of the different nitrates was made possible.

Solutions of the alkali nitrates have been studied by Carelli, Pringsheim and Rosen,[3] who obtained only one strong line (1040^{-1} cm.) and identified it with the inactive frequency of the NO_3 ion. Ca and NH_4 nitrate solutions were examined later by Dickinson and Dillon,[4] who obtained two lines (1052 and 723^{-1} cm.) one of which was strong and the other faint. Schaefer, Matossi and Aderhold[5] have examined a single crystal of $NaNO_3$ and recorded the presence of five Raman lines three of which they attributed to the NO_3 ion. Menzies noticed a single line (1052^{-1}cm.) with coarsely powdered crystals of KNO_3. Bar also observed a single line with $NaNO_3$ (1074) and two with NH_4NO_3. The latter author as well as Schaefer have remarked on the large change in the value for the inactive frequency of the NO_3 ion when passing from the solid state to solution. In the present investigation, in addition to several inorganic nitrates in the solid state, the case of lithium nitrate has also been examined in a concentrated aqueous solution. In the case of $NaNO_3$ four out of the five lines obtained by Schaefer with a single crystal were obtained without any difficulty with an aggregate composed of small crystals. Lithium nitrate showed an equal number of lines but it was difficult to get some of the lines sharp with the higher nitrates.

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[1] Nature, Oct. 5, 1929, [2] Nature, Nov. 2, 1929.

[3] Carelli, Pringsheim and Rosen, Z. f. Phys., 51, 511, 1928.

[4] Dickinson and Dillon, Proc. Nat. Acad. Sci., March, 1929.

[5] Schaefer, Matossi and Aderhold, Phys. Zeit., **30**, 581, (1929)

Experimental Arrangements.

A Cooper-Hewitt quartz mercury lamp working at 4-5 amperes was used as the source of illumination. A slow current of air was directed on to the lamp from a fan, which prevented its getting excessively hot. Under these conditions, it was found that the lamp emitted much less continuous spectrum. The spectrograph used was a Fuess glass prism instrument of large dispersion which gave nearly 24 A per mm. in the region of 4600 A.

The substance under investigation was enclosed in a triangular shaped cell (capacity about 60 c. c.) two sides of which were silvered, the incident light entering through the third. The mercury arc was placed immediately over the cell, and the scattered light emerging from one of the triangular sides was concentrated on the slit of the spectrograph, the opposite side of the cell being blackened. With this arrangement, a very efficient illumination of the crystals was obtained, the scattered light undergoing reflection not only by the crystals but also by the walls of the container. The substance in the form of small crystals or irregular crystalline aggregates (only Kahlbaum's or Merck's extra pure chemicals were used) was transferred directly to the cell, big lumps however being broken into smaller ones. A smaller cell was used in cases where a larger quantity of the substance was not available and also when it was finely divided. Using Ilford Iso-Zenith plates, exposures ranging from $\frac{1}{2}$—1 hour were sufficient for each spectrogram. In some cases, a concentrated didymium chloride solution in a glass container was placed between the mercury arc and the cell. This reduced the continuous spectrum considerably, and served to bring out the fainter lines. An iron arc comparison spectrum was recorded on each plate and the positions of the Raman lines were obtained by linear interpolation from the nearest known iron lines.

Results.

Nineteen inorganic nitrates were examined, some in the anhydrous condition and others as hydrates. The substances were of Kahlbaum's or Merck's origin which were used as such, except Pb and K nitrates which were recrystallised from water. The wavelengths and frequency shifts of the Raman lines are set forth in the following tables. Table I shows the values for the inactive frequency of the NO_3 ion which appears as a strong Raman line. Tables II and III give measurements for two of the active frequencies which also appear in infra-red absorption, *viz.*, those corresponding to about 7μ and 13—14μ. In the latter region only one frequency could be observed, though it is known from infra-red measurements that two exist. Table IV gives values for the Raman lines corresponding to absorption in the remote infra-red, which were observed only with four substances. Its presence in other nitrates is doubtful. Table V summarises the results for the alkali nitrates. The values observed by Schaefer and Schubert from infra-red measurements are also set forth in the tables in appropriate places.

TABLE I.

Nitrate of	Wavelength λ in A.	Wave No. ν	Frequency Shift.	Infra-red in μ.	Description of Substance.
Lithium Soln.	4567·61	21887·0	1049·7	9·527	Merck's pure sample. Saturated aqueous soln.
Lithium Cryst.	4571·70	21867·6	1069·1	9·354	,, $LiNO_3 + 30\% H_2O$
	4566·04	21885·1	1051·6	9·509	
Sodium	4571·04	21870·7	1066·0	9·381	Kahlbaum. Anhydrous.
Magnesium	4569·65	21877·4	1059·3	9·440	Merck. $Mg(NO_3)_2 + 6H_2O$.
Strontium	4569·06	21880·2	1056·5	9·465	Kahlbaum. $Sr(NO_3)_2 + 4H_2O$.
Potassium	4567·93	21885·6	1051·1	9·514	,, Anhydrous
Cadmium	4567·92	21885·7	1051·0	9·515	Merck. $Cd(NO_3)_2 + 4H_2O$.
Beryllium	4567·76	21886·5	1050·2	9·522	Kahl. $Be(NO_3)_2 + 3H_2O$ Deliquescent.
Barium	4567·15	21888·0	1048·7	9·536	Merck. Anhydrous.
Aluminium	4567·29	21888·7	1048·0	9·542	,, $Al_2(NO_3)_6 + 1\ H_2O$
	4569·31	21879·0	1057·7	9·454	
Calcium	4567·05	21889·7	1047·0	9·551	,, $Ca(NO_3)_2 + 38\% H_2O$.
Lead	4567·04	21889·9	1046·8	9·553	Merck. Anhydrous.
Silver	4566·66	21891·9	1044·8	9·571	,, ,,
Zinc	4566·15	21892·7	1044·0	9·579	,, $Zn(NO_3)_2 + 20\% H_2O$.
Ammonium	4566·24	21893·7	1043·0	9·588	Kahl. Anhydrous.
Mercurous	4566·04	21894·7	1042·0	9·597	,, $HgNO_3 + H_2O$.
Manganese	4565·69	21896·4	1040·3	9·613	Merck. $Mn(NO_3)_2 + 4H_2O$.
Thorium	4565·21	21898·5	1038·2	9·632	Kahl. $Th(NO_3)_4 + 1H_2O$.
Mercuric	4565·14	21899·0	1037·7	9·637	Merck. Deliquescent.
	4561·66	21915·7	1021·0	9·794	
Bismuth	4564·97	21899·8	1036·9	9·644	Kahl. $Bi(NO_3)_3 + 5H_2O$.

in the form of small crystals or irregular crystalline aggregates (only Kahlbaum's or Merck's extra pure chemicals were used) was transferred directly to the cell, big lumps however being broken into smaller ones. A smaller cell was used in cases where a larger quantity of the substance was not available and also when it was finely divided. Using Ilford Iso-Zenith plates, exposures ranging from ½—1 hour were sufficient for each spectrogram. In some cases, a concentrated didymium chloride solution in a glass container was placed between the mercury arc and the cell. This reduced the continuous spectrum considerably, and served to bring out the fainter lines. An iron arc comparison spectrum was recorded on each plate and the positions of the Raman lines were obtained by linear interpolation from the nearest known iron lines.

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Beryllium	4567·76	21886·5	1050·2	9·522	Kahl. $Be(NO_3)_2 + 3H_2O$ Deliquescent.
Barium	4567·45	21888·0	1048·7	9·536	Merck. Anhydrous.
Aluminium	4567·30	21888·7	1048·0	9·542	,, $Al_2(NO_3)_6 + 18H_2O$
	4569·31	21879·0	1057·7	9·454	
Calcium	4567·08	21889.7	1047·0	9·551	,, $Ca(NO_3)_2 + 38\% H_2O$.
Lead	4567·01	21889·9	1046·8	9·553	Merck. Anhydrous.
Silver	4566·63	21891·9	1044·8	9·571	,, ,,
Zinc	4566·45	21892·7	1044·0	9·579	,, $Zn(NO_3)_2 + 30\% H_2O$.
Ammonium	4566·24	21893·7	1043·0	9·588	Kahl. Anhydrous.
Mercurous	4566·04	21894·7	1042·0	9·597	,, $HgNO_3 + H_2O$.
Manganese	4565·69	21896·4	1040·3	9·613	Merck. $Mn(NO_3)_2 + 4H_2O$.
Thorium	4565·24	21898·5	1038·2	9·632	Kahl. $Th(NO_3)_4 + 4H_2O$.
Mercuric	4565·14	21899·0	1037·7	9·637	Merck. Deliquescent.
	4561·66	21915·7	1021·0	9·794	
Bismuth	4564·97	21899·8	1036·9	9·641	Kahl. $Bi(NO_3)_3 + 5H_2O$.

TABLE II.

Nitrate of	Wavelength λ	Wave No. ν	Frequency Shift.	λ_R in μ.	Reflection maxima in μ.
Lithium ...	4501·4	22209·1	727·6	13·74	......
Sodium ...	4499·8	22217·0	719·7	13·89	14·44
Potassium ...	4498·1	22225·4	711·3	14·06	15·14
Ammonium ...	4497·7	22227·4	709·3	14·10	......
Strontium ...	4502·5	22203·7	733·0	13·64	......
Barium ...	4501·6	22208·1	728·6	13·72	13·74
Lead ...	4501·4	22209·1	727·6	13·74	13·94

TABLE III.

Lithium ...	4639·9	21546·2	1390·5	7·192	......
Sodium ...	4638·3	21553·6	1383·1	7·230	7·12
Potassium ...	4631·3	21586·2	1350·5	7·405	7·18
Lead ...	4638·0	21555·0	1382	7·24	7·72
Barium ...	4641·0	21541·0	1396	7·17	7·30
Silver ...	4636·0	21564·3	1372	7·29	7·45

TABLE IV.

Lithium ...	4403-3	22703·9	232·9	42·94	
Sodium ...	4393·9	22752·5	184·2	54·29	
Mercurous ...	4391·0	22762·8	173·9	57·50	
Lead ...	4388·2	22782·0	154·7	64·64	

TABLE V.

Nitrate of	Frequency Shift F_1	F_2	F_3	F_4
Lithium	1069·1 1051·6	727·6	1390·5	232·9
Sodium	1066·0	719·7	1383·1	184·2
Potassium	1051·1	711·3	1350·5	......
Ammonium	1043·0	709·3	......	......

It will be seen from Table I that in the case of Li, Al and Hg (ic) nitrates a faint companion is present along with the prominent line. A photograph taken with a concentrated solution of lithium nitrate, however, did not show this component. Its presence seems to be a consequence of the crystal structure, and its probable origin will be discussed in the following pages.

Discussion of Results.

X-ray investigations of calcite show that the CO_3 ion can be pictured as a plane equilateral triangle, the oxygen atoms occupying the corners while the C atom occupies the centre. The possible number of vibrations of this group has been worked out theoretically by Kornfeld[1] and by Brester,[2] who obtain four frequencies one of which should be inactive. The latter corresponds to a symmetrical vibration of the three oxygen atoms towards and away from the central atom, producing no change in the electric moment. Two more are associated with vibrations in the plane involving change in the electric moment. The vibration corresponding to about 15μ is due to the movement of any one oxygen along the median followed by a small alternate elongation and diminution of the opposite side of the group, while that at about 7μ is due to the oscillation of the carbon atom along or perpendicular to any median. The fourth frequency (at about 11μ) is attributable to the vibration of the central atom at right angles to the plane. Since $NaNO_3$ is almost identical in structure with $CaCO_3$ as shown by X-ray analysis, similiar vibrations can be supposed to take place in the NO_3 ion. Exactly in accordance with this hypothesis, the infra-red reflection measurements of Schaefer and Schubert[1] on the metallic nitrates indicated the presence of three active fundamentals corresponding roughly to 7, 15 and 12μ respectively. Experiments using polarised light also showed that absorption at 12μ was due to vibrations taking place at right angles to the plane containing the atoms, while the other two were due to vibrations in the plane. Later infra-red absorption measurements of Schaefer, Matossi and Dane showed a large number of maxima, which, in addition to fundamentals and overtones, were also due to combinations of the fundamental frequencies. The authors found it necessary to postulate the presence of an inactive frequency at about 10μ to explain all their combination frequencies, and this agreed very well with the theoretical considerations of Kornfeld and Brester. This assumption was later beautifully verified by the Raman spectra of the carbonates and nitrates, which showed up this inactive frequency very strongly.

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[1] Kornfeld, Z. f. Phys., 26, 205, (1924).

[2] Brester, Z. f. Phys., 24, 324, (1924).

The early measurements of Schaefer and Schubert with the inorganic nitrates showed a slight slowing down of the oscillations with an increase in the atomic weight of the metal ion of the crystal. In the present investigation, this effect could be observed accurately in the case of the inactive frequency which always appeared as a strong Raman line in all the spectrograms. A glance at Table I will show that the

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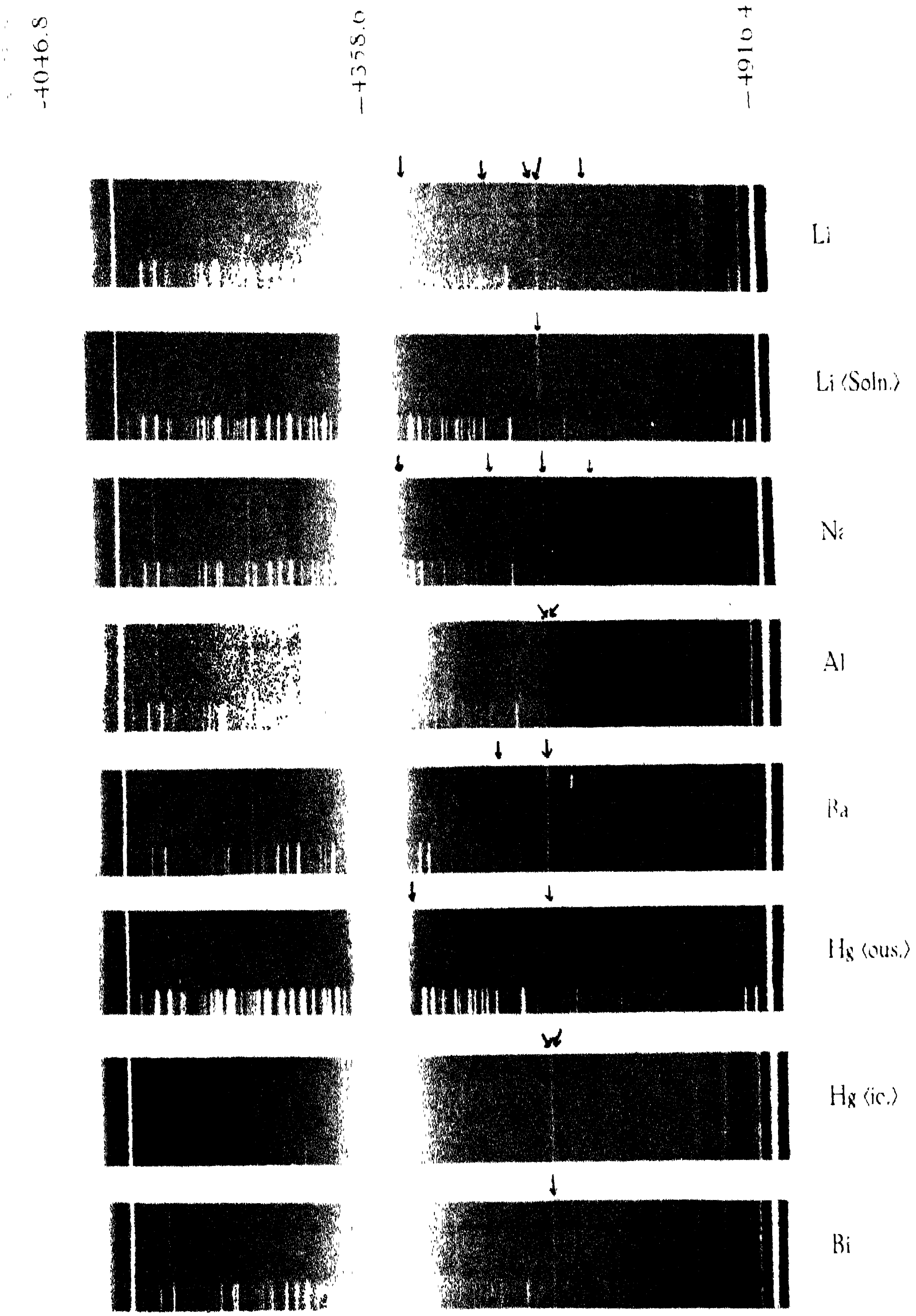
[1] Schaefer and Schubert, Ann. d. Phys., 55, 577 (1918).



Raman Spectra of Inorganic Nitrates

light metals are at one end and the heavy ones at the other, showing the slowing down of the oscillation frequency with increase in atomic weight of the metal ion. Comparing the value for this frequency in every case with that observed in solution (1050^{-1} cm.), it will be found that Li, Na and Mg nitrates show a considerably larger frequency shift (max. value, 1069 wave nos.), Th, Hg and Bi show a smaller shift (min. value, 1037), while Ca, Ba, Pb, K, Al, Cd, Ag show intermediate values. In order to explain most of the observed facts, the view is here put forward that in the fully ionised crystals, the influence of the metal ion on the vibrations of the nitrate ion is proportional to the volume occupied by the metal ion in the crystal lattice. The smaller the volume the greater the characteristic oscillation frequencies associated with the NO_3 group and *vice versa.* This is shown by the regular sequence in the alkali nitrates (Table V) and in Ba and Pb nitrates.

There is another characteristic feature about the Raman line corresponding to the inactive frequency, as mentioned previously. This is the appearance of a fainter component in the case of Li (1052 wave nos.), Hg (ic) (1021) and Al (1058) nitrates. In the first two cases, it is very faint and appears to the short wave length side of the principal line, while with Al it is present on the opposite side. In the case of lithium nitrate this component does not occur in a concentrated solution, and as such it seems to be associated with the crystal structure of the substance. We have also seen how the position of the principal line is influenced by the volume occupied by the metal ion in the lattice. The view is now put forward that the fainter component is due to the *polymerised* molecule in the solid state, probably dimeric, the intensity of the component being a measure of the strength of the bond between the metal ions themselves. In other words, the fainter line represents the inactive frequency of the NO_3 ion as influenced by Li_2, Hg_2 and Al_2

respectively. We know that in the case of aluminium nitrate, the formula is usually represented as $Al_2(NO_3)_6$, $18H_2O$ instead of the simpler one. Another fact which seems to support this view is that Li and Hg (ic) nitrates form stable crystals with water content amounting to $\frac{1}{2}H_2O$. This necessarily means that in the crystal lattice of these substances the nitrates have to exist as $Li_2(NO_3)_2,H_2O$ and $Hg_2(NO_3)_4$, H_2O. The NO_3 ion is now influenced by Li_2 and Hg_2 respectively, and hence the prominent frequency associated with it should show a shift to the short wavelength side of the prominent line, which is actually observed to be the case. According to this view, the stronger line in aluminium nitrate should be due to the polymerised molecule, and the fainter line to the simple one.

Coming to a consideration of the active frequencies of the NO_3 ion, we find that only two out of the three frequencies recorded by infra red measurements appear as Raman lines. Probably one of the lines is too feeble for measurement. The faint line (about 720^{-1} cm.) is fairly sharp, and it will be taken up first for consideration.

It will be seen at once from Table II that the substances fall into two groups if we arrange them in the order of increasing atomic weight of the metal atom. The alkali metals show the line at 728, 720, 711 and 709^{-1} cm. for Li, Na, K and NH_4 nitrates, respectively. This is to be expected since the volume occupied by the metal ion increases from member to member, and causes a slowing down of the characteristic oscillation frequency. But with Ba and Pb nitrates, lines corresponding to about 728^{-1} cm. were observed, showing a larger frequency shift, whereas we should expect the reverse change. Hence it is concluded that the frequencies observed with alkali nitrates are different in origin from those observed with Sr, Ba and Pb nitrates. In the former they are due to vibrations in the plane of the NO_3 group, while in the latter they probably represent vibrations of the N at right angles to the plane. The question may then arise why the latter frequency appears with Ba and Pb nitrates but not with the alkali nitrates. We know in the case of the uniaxial crystal of $NaNO_3$, the vibration of the N atom at right angles to the plane will appear strongly only when excited in a direction along the optic axis. In other cases, especially when the crystals are oriented at random as in the present experiment, it is likely to be feeble. The possibility of exciting that vibration is greater with the isotropic crystals of Ba and Pb nitrates, and hence the Raman line at 13·7μ in the latter is attributable to the vibrations of the N perpendicular to the plane of the group. This conclusion is in agreement with infra-red reflection measurements of Schaefer and Schubert who find a maximum at about 13·5μ with Ba and Pb nitrates, the other one corresponding to vibrations in the plane occurring at about 15μ.

The maxima observed at about 7μ in the infra-red reflection spectra of the nitrates are shown as sharp Raman lines with Li and Na nitrates in approximately the same position, but with KNO_3 it appears as a broad line shifted to shorter wavelengths. With the higher nitrates, only a broad band in a similar position is observed. It should be noted here that Schaefer's measurements in the infra-red show this to be a broad region of absorption, and further, the position of the maximum shifts slightly with the three different directions in a biaxial crystal.

We have still to consider the origin of the Raman lines corresponding to a characteristic frequency in the remote infra-red. These lines have been observed with calcite, but they are not found in a solution of K_2CO_3.[1] This observation shows that the vibrations are connected with the crystal lattice. They probably involve mutual swingings of the Ca and CO_3 ions in the lattice. In the present investigation, Li and Hg (ous) nitrates showed a prominent line (43 and 58μ *respectively*). Sodium and lead nitrates showed broader and *fainter lines*. But it is interesting to note (Table IV) that the *position of this line, whenever observed, seems to depend on the atomic weight* of the metal atom, in agreement with the view that it is due to the oscillation involving the metal ion and NO_3 ion in the lattice. This line disappears in the case of lithium nitrate in a concentrated aqueous solution, showing thereby that the crystalline state is essential for maintaining such an oscillation.

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[1] Leontowitsch, Z. f. Phys., 54, 155, (1929).

Conclusion.

It will be seen that the powder method of investigating the Raman effect opens up a wide field for research, as this preliminary investigation will show. The material to be examined can be in any form whatever, and the time taken for the examination of each substance is reasonably short. Experiments are in progress with an instrument of larger dispersion to determine the fine structure of the Raman lines in crystal powders. Various types of inorganic compounds are also under investigation to correlate the Raman lines with their structure and to supplement the existing data regarding the position and orientations of the molecules, atoms or ions in the crystal lattice by this powerful method of analysis.

I wish to thank Professor Sir C. V. Raman, F.R.S., for suggesting this problem, and for his constant help and guidance during the course of this investigation.

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2

Raman Effect in Some Organic and Inorganic Substances

By

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(Plates II and III).

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Abstract.

The paper describes the results of a study of the Raman spectra of several organic and inorganic substances, namely urea, ethyl formate, ethyl malonate, ethyl acetoacetate, ethyl monochloroacetate, ethyl carbonate, potassium and ammonium thiocyanates, phenyl isothiocyanate, potassium cyanide, potassium cyanate, double cyanide of silver and potassium, methyl cyanide, aniline, phenylhydrazine, hydrazine hydrate, benzaldehyde and formaldehyde.

Aniline and phenyl hydrazine darken in air under the action of light, thus rendering the study of the scattering of light in them extremely difficult. The difficulty has been successfully overcome by distilling these liquids into the observation tube in vacuo. Under these conditions, the liquids do not develop colour and the Raman lines come out strongly, unaccompanied by a continuous spectrum. Other liquids, *e.g.*, benzaldehyde, give a continuous spectrum even in the absence of air.

The cyanides give two Raman frequencies of about 886 and 2080 which are presumably characteristic of the cyanogen ion. It is remarkable that

the frequency 756 appearing in phenyl isothiocyanate which may be attributed to C=S does not differ appreciably from that of C—S in the thiocyanates, *viz.*, 741.

It is suggested that the production of continuous spectrum accompanying the Raman lines is due to the photochemical action of the light causing the molecules themselves (or their reaction products) to dissociate into parts having a distributed range of kinetic energies.

1. *Introduction.*

The discovery of the Raman Effect, apart from its theoretical importance, has opened up a new method of investigating molecular spectra in the infra-red region with comparative ease and accuracy. A large number of substances has already been investigated for their Raman scattering and an attempt has been made to determine the influence of chemical structure upon the Raman spectra. It has been found that, although each substance shows its own characteristic Raman spectrum, certain similarities are noticeable in the spectra of compounds having similar chemical composition. For instance, it has been found that all aromatic compounds containing a carbon-hydrogen linkage, show prominently a modified line in identically the same position, corresponding to the frequency shift 3060 wave numbers, which has therefore been identified to be the natural frequency of the aromatic C-H bond. Similarly the frequency 2940 has been identified as due to the oscillation of the aliphatic C-H bond. Ganesan and Venkateswaran,[1] and recently Dadieu and Kohlrausch[2] have carried out elaborate investigations of the Raman spectra of a large number of substances from this point of view and have been able to isolate the oscillation frequencies of a number of chemical bonds.

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[1] Ind. Journ. Phys., Vol. IV, p. 195, 1929.

[2] Sitz. Akd. Wiss. Wien, Vol. 138, pp. 41, 335, 419, 607, 635.

The present paper describes an investigation of the Raman spectra of a number of organic and inorganic substances and a discussion of the results in relation to their chemical structure. The paper also contains a description of a new method of studying the Raman spectra of liquids that rapidly darken in air under the action of light.

2. *Experimental Method.*

The investigation was carried out by an arrangement similar to the one described by Wood.[1] A quartz mercury vapour lamp of 3000 C.P., made by Heraus, was used as the source of illumination and the spectrum of the scattered light was taken with a Constant Deviation Spectrograph, using Ilford's Iso-Zenith (H &D 700) or Soft-Gradation Panchromatic plates. The time of exposure varied from one to six hours for different substances. Kahlbaum's pure substances and in some cases Merck's extra pure chemicals were used. Further purification was made, wherever found necessary, in the way indicated later on. The wave lengths were calculated by Hartmann's simplified interpolation formula, using the mercury lines as standards for reference and in some cases by means of a copper comparison spectrum.

3. *Results.*

Urea. (TABLE I).

Saturated solution of urea in water was investigated for its Raman scattering. It gives a number of lines, of which those corresponding to the frequency shift of 1000 wave numbers are very prominent. The origin of this frequency is not understood.

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[1] R. W. Wood, Phil. Mag., Vol. VI, p. 729, Oct. 1928.

Esters. (TABLES II-VI).

Five esters have been studied, namely, ethyl formate, ethyl malonate, ethyl acetoacetate, ethyl monochloroacetate and ethyl carbonate. In all of them the modified lines corresponding to the Raman shifts 2930 and 2970 come out very prominent. As a close companion of this group there also appears a weak line corresponding to the shift 2878. There is a small continuous spectrum present in the scattering by most of the esters; which is particularly marked in ethyl malonate and ethyl acetoacetate.

Potassium and Ammonium Thiocynates and Phenyl Isothiocyanates.

(TABLES VII AND VIII.)

Saturated aqueous solutions of potassium and ammonium thiocyanates have been investigated. Both of them show eight modified lines in exactly the same positions, corresponding to the frequency shifts 2060 and 738; which are evidently due to the -S-C-N ion. The lines corresponding to the shift of 2060 come out to be very prominent; in fact the one excited by 4358 A.U. is even stronger than the mercury line 4916 A.U. appearing on the plate.

In order to investigate the influence of isomerism of the SCN group on its Raman frequencies, freshly distilled phenyl mustard oil was studied. As many as 24 lines have been obtained some of which are sufficiently strong to be seen visually through the spectroscope. Several of them coincide in position with the lines of the benzene spectrum, and are evidently due to the phenyl group. Among the other Raman radiations of this liquid, the broad band corresponding to a shift of about 2056 wave numbers, and the line shifted by 756 may be specially mentioned as they seem to have their origin in the $-N=C=S$ group.

PAL & SEN GUPTA

PLATE II

Raman Spectra

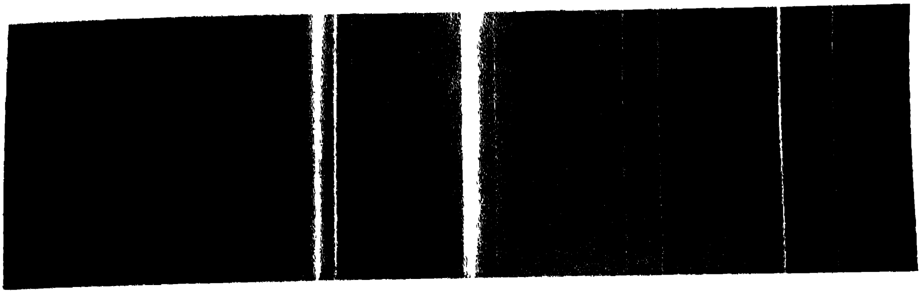

Fig. 1

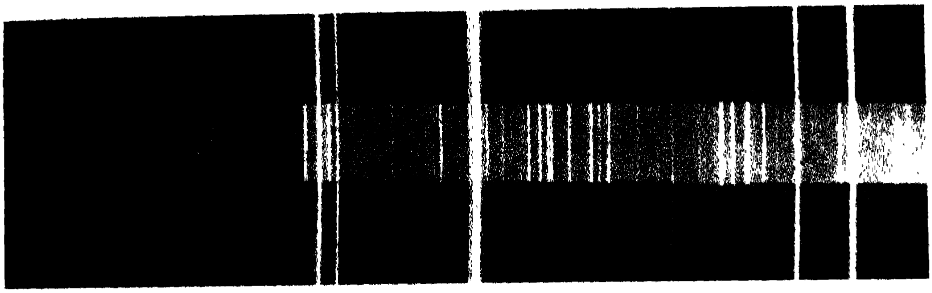

Fig. 2

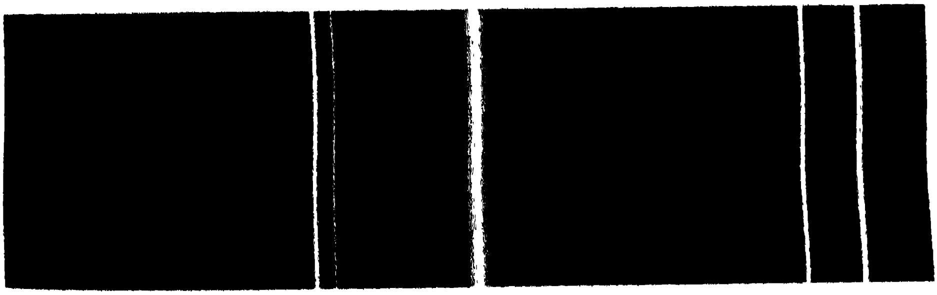

Fig. 3

Fig. 1—Potassium thiocyanate   Fig. 2—Acetonitrile   Fig. 3—Aniline

Cyanides and Cyanates (Tables IX-XII)

Potassium cyanide and cyanate were studied in solution in water, and double cyanide of silver and potassium in solution containing slight excess of KCN; one organic cyanide was also investigated *viz.*, methyl cyanide.

Potassium cyanide gives two Raman frequencies 836 and 2080 which are presumably due to the CN ion; these frequencies appear also in the scattering by the other substances, but in slightly different positions. Potassium cyanate has, in addition two other frequencies, 1229 and 1314, while methyl cyanide shows several.

Aniline (Table XIII)

The fact that aniline quickly darkens in air under the action of light with the consequent absorption in the violet, renders the study of its Raman scattering extremely difficult. Owing to this cause, Fujioka[1] was not able to obtain any Raman lines at all with this liquid. Dadieu and Kohlrausch[2] and Bonino and Brull[3] used freshly purified aniline and changed the liquid every fifteen minutes. Even with these precautions the Raman lines which they obtained were very faint. On the other hand we find that if the liquid is distilled and studied for its scattering in vacuum, it does not show any appreciable tendency to darken even after several hours exposure to the light of the mercury arc. In our investigations with this and other similar liquids, a distilling flask was attached to the horn end of the Wood's tube. After introducing the necessary amount of liquid the apparatus was connected to a pump and while it was being exhausted, the liquid was kept boiling vigorously to drive off traces of air from the apparatus; it was then sealed off from the pump. The liquid was then distilled over to the Wood's tube and after washing the latter with the distillate once or twice and transferring back to the flask it was allowed to fill it up. The distilled aniline was perfectly colourless, and remained so even after three hours exposure to the intense light of the arc used for the investigation of its scattering. Under these conditions the Raman lines of aniline came out very prominently with no trace of the continuous spectrum, which is so conspicuous in the scattering of aniline when it is kept exposed to air.

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[1] Inst. Phys. Chem. Research. Tokyo, Vol. 11, pp. 205-222, 1928.

[2] Sitz. Akd. Wiss. Wien., Vol. 138, p. 341, 1929

[3] Gazetta Chemica Italiana, Vol. 59 p. 668, 1929

Phenyl Hydrazine (Table XIV)

Like aniline phenyl hydrazine also quickly gets coloured in air under the action of light. We therefore, studied its scattering by the same method as described in the case of aniline. The liquid was distilled in vacuum at about 150-155°C. and a slightly straw coloured liquid was obtained in the Wood's tube. A good spectrogram was obtained on a three hours exposure, with no appreciable amount of continuous spectrum. The liquid did not darken even on a very long exposure. As many as 18 lines have been obtained some of which are very prominent and coincide in positions with those in aniline.

Hydrazine Hydrate (Table XV)

A 90% solution of hydrazine in water was studied. A few lines which are more or less diffuse, have been obtained upon a continuous background. There is a close doublet corresponding to frequency shifts 3215·75 wave numbers.

Benzaldehyde (Table XVII)

Benzaldehyde[1] offered the same difficulties as experienced in the case of aniline, and the same method was therefore adopted for its investigation. The liquid was distilled in vacuo at 120°C., and a perfectly colourless distillate was collected in the Wood's tube. We have obtained as many as 37 lines which are very sharp and some of them very intense. The sharpness of the modified lines seems to be a remarkable characteristic of this liquid. In this particular case, however, the exclusion of all traces of air does not seem to prevent completely the darkening of the liquid under the influence of the intense light of the arc. There is always an appreciable continuous background in the scattered spectrum, which seems to get more and more prominent as the liquid darkens.

Formaldehyde (Table XVI)

An 80% aqueous solution of formaldehyde was used for the investigation. A number of lines have been obtained which are more or less diffuse.

4. *Discussion of Results.*

It has already been mentioned in the introduction that associated with each type of chemical bond, there appear in the various molecules containing such a bond certain well-defined Raman frequencies characteristic of it. Probably, the best example of such a persistence of the frequencies in different compounds where the same group appears, is afforded by a study of the various derivatives of benzene. Almost all the lines appearing in the scattering by benzene liquid are

[1] Sitz. Akd. Wiss. Wien, Vol. 138 p. 340, 1929

also present in general in that of all the aromatic compounds, as can be easily seen from the Tables given in the previous section.

An equally striking example is the prominent group of three frequencies, 2878, 2930 and 2970, which are common to all the ethyl esters. This group has been identified by Ganesan and Venkateswaran[1] as due to the aliphatic C-H linkage and they further point out that as we proceed to higher members in any series of aliphatic compounds containing hydrogen this group becomes more complex, splitting in some cases into as many as five components more or less equally spaced. In connection with this remark it is significant that in the case of the simple compounds like methyl cyanide and formaldehyde which have been investigated by us there is only one line representative of this group. The frequency 1140 always accompanies the above group of lines and is presumably also to be attributed to the same origin.[2] Corresponding to the above group of lines in the aliphatic series, the aromatics also show a line at about 3060 due to the aromatic C-H bond.

In view of the appreciable difference in frequency of oscillation of the aliphatic and aromatic carbon atoms, we would naturally expect the frequencies corresponding to a linkage between any two given atoms to be widely different, according as the bond between them is single, double or triple. But the results obtained with $-S-C\equiv N$ and $S=C=N-$ gives us a pause here. The frequency 756 in phenyl mustard oil which is presumably due to $C=S$ bond, as is evidenced by its appearance also in CS_2,[3] does not differ appreciably from that of the C-S bond in the thiocyanates, *viz.*, 741. Regarding the linkage between the C and N atoms, however, though the absolute value of the frequency does not seem to depend on whether the bond is triple or double, the spectral characters of the radiations corresponding to the two bonds seem to be quite different; whereas in the former case, *i.e.*, $C\equiv N$, the radiation is very sharp, (not only in the case of the thiocyanates but also in the scattering by the cyanides and cyanates investigated by us) the double bonded $C=N$ of phenyl mustard oil gives a very broad band extending over nearly 120 wave numbers.

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[1] Ind. Journ. Phys., Vol. IV, pp. 195-280, 1929.

[2] Sitz. Akd. Wiss. Wien. Vol. 138, p. 607, 635, 1929.

[3] Ind. Journ. Phys., Vol. IV, p. 253, 1929.

The statements made in the previous paragraphs may suggest that the Raman lines corresponding to $C\equiv N$ appear in the same position in the various cyanides cyanates, and thiocyanates. Strictly speaking, it is far from being the case. They vary to some extent from compound to compound which is probably what is to be expected, since the oscillation of a bond will not be quite unaffected by the positions and masses of the neighbouring atoms of the molecule. But if this were the explanation, we should further find that in the simplest case of the $C\equiv N$ ion in potassium cyanide solution, the frequency should be the one really characteristic of the bond, and that in other cases, *e.g.*, $Ag(CN)_2$ ion, due to the loading of either of the atoms C and N by the neighbouring ones, the frequency of oscillation must be diminished. But as a matter of fact the reverse is the case. The frequency of the $C\equiv N$ bond is almost a minimum in the case of KCN and greatest in the case of acetonitrile, $KAg(CN)_2$ coming intermediate. The exact significance of this order is difficult to understand.

Finally we come to the N-H bond. The frequency 3358 in aniline, that of the doublet 3215, 3275 in hydrazine hydrate, and 3226 and 3374 in urea are attributable to it. In support of this assignment of frequencies we may evidence the results obtained by Carelli, Pringsheim, and Rosen[1] on light scattering by solution of ammonia in water which gives also two frequencies in comparable positions, *viz.*, 3331 and 3389. The singlet value of this frequency in some compounds, *e.g.*, aniline, and its duplexity in others are probably to be attributed to the same cause which determines the complexity or otherwise of the analogous C—H bond in the different aliphatic compounds discussed in an earlier part of this section.

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[1] Zeits. f. Phys. Vol. 51, p. 511, 1928.

5. *Continuous Spectrum.*

We should add a few words regarding the continuous spectrum that generally appears in the scattered spectra of most of the substances studied for their Raman scattering. That it is really a characteristic of the substance and not due to impurities is evident from the fact that it is exhibited by even the purest liquid, purified by a slow distillation in vacuum. Venkateswaran [1] tried to connect it with the viscosity of the substance. During our investigations with aniline, phenyl hydrazine, benzaldehyde, guanidine, etc., we have been led to form a different view of the phenomena. We have observed that the continuous spectrum is markedly developed in substances which are sensitive to light; the presence of photochemical changes being in most cases evident by the change of colour of the substance during an exposure. In some cases the induced changes require the presence of air and the continuous spectrum in those cases increases in intensity with time, *i.e.*, with the increase of concentration of the intermediate compound. There is, however, a further category in which light can act on the substance directly and changes seem to proceed even in vacuum. We have observed that in certain cases the continuous spectrum may be almost completely suppressed by removing air, as in the case of aniline and phenyl hydrazine. In the case of benzaldehyde, however, we have found that the changes in colour go on even in vacuum and we have convinced ourselves, by taking different exposures, that the continuous spectrum does actually increase with time, *i.e.*, with the increased concentration of the product of photochemical reaction.

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[1] Ind. Journ. Phys., Vol. III, p. 105, 1928.

In the case of aqueous solutions of certain substances which are not appreciably viscous we have also found the continuous spectrum developed in considerable intensity. The case of guanidine is very characteristic : even a moderate concentration introduces an intense continuous spectrum.

We suggest a mechanism of the production of the continuous spectrum, somewhat on the same lines as the explanation of the continuous spectrum in hydrogen given by Blackett and Franck.[1] Either the molecule itself or the product of the photochemical reaction can go to an excited state involving large electronic energy change ; the total energy thus absorbed exceeds the energy of molecular dissociation by a large amount. It is then clear that the final state may be a dissociated molecule with parts having various kinetic energies relative to one another. The initial state is discrete, whereas, the final state corresponds to continuously distributed energy levels. The resultant radiation will thus have a sharp violet edge and will continue far in the red end, which is usually observed in most cases.

The absence of continuous spectrum in aniline, etc. may be explained by saying that it is the first product of reaction which further breaks down under the action of light. The absence of air suppresses the first chemical reaction and suppresses the continuous spectrum also. In other molecules, the action of light may consist in an immediate partial disintegration of the molecules even in vacuum, or the photochemically sensitive product may not depend upon the presence of air at all for its formation. In this connection it is interesting to note the similarity of our explanation with the ideas of Perrin[1] about the origin of fluorescence.

---

[1] Zeits. f. Phys., Vol. 34, p. 389, 1925.

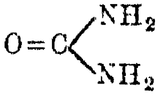
Since the paper was sent to press we have been studing in detail the Raman Spectra of liquids like benzaldehyde which darken under the action of light even in vacuum. By maintaining a continual flow of distilled liquid through the Wood tube (which is done with the help of a specially constructed distillation apparatus) we have been able to completely eliminate the continuous spectrum. The details of the experimental arrangement and the significance of the results obtained to the explanation of the continuous spectrum briefly outlined in this paper, are reserved for separate publication.

In conclusion we wish to express our sincerest thanks to Prof. S. N. Bose for his kindly suggesting the problem and helpful guidance during the progress of the work. Our thanks are also due to Mr. K. S. Krishnan for his many valuable suggestions and kind interest in the work.

PHYSICS LABORATORY
DACCA UNIVERSITY,
8th April, 1930.

TABLE I.

Urea.



$O{=}C\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. $\Delta\nu$
(2)	21331	24705	3374
(1)	21479	,,	3226
(0)	21774	22938	1164
(5)	21938	,,	1000
(2)	22108	,,	830
(0)	23545	24705	1160
(5)	23702	,,	1003

$\Delta\nu$: 830, 1002, 1162, 3226, 3374.

---

[1] Ann de Phys. Series 9, Vol. 10, page 138, 1918.

Raman Spectra

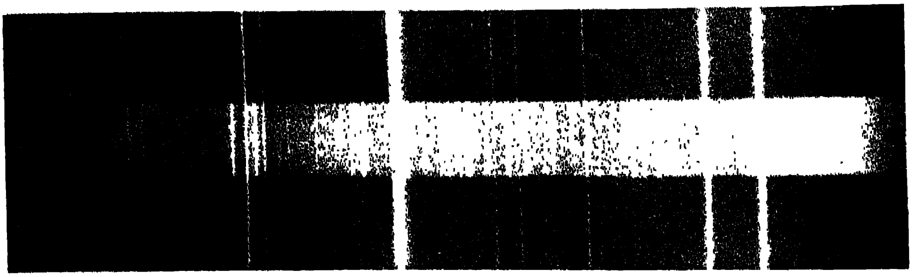


Fig. 4

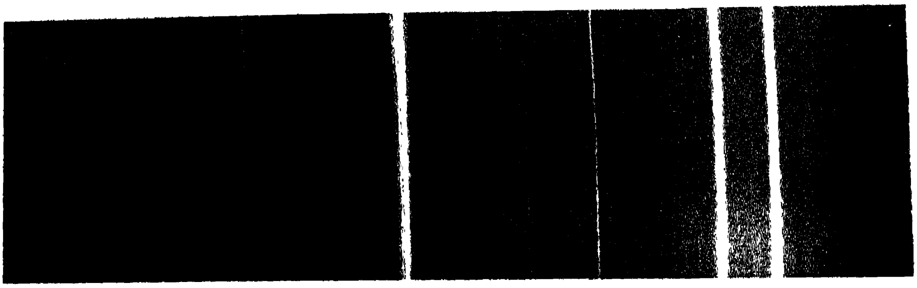


Fig. 5

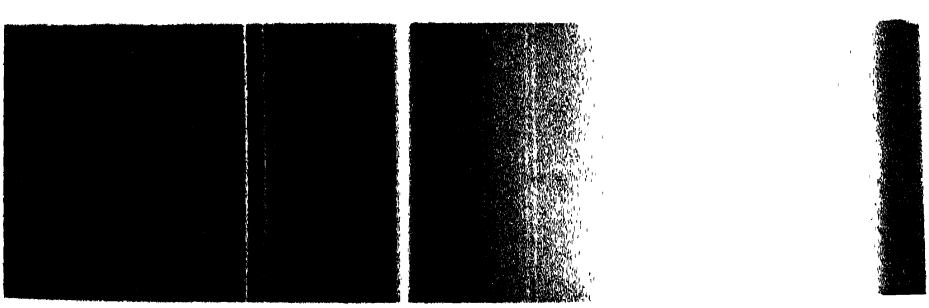
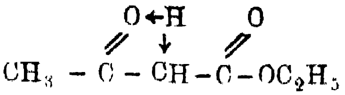


Fig. 6

ig. 4 – Phenyl Mustard Oil – Phenyl hydrazine Fig. 6 – Benzaldehyde

TABLE II.

Ethyl Acetoacetate



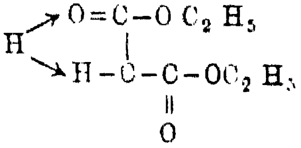
$$\begin{array}{l} \qquad\quad\;\; O \leftarrow H \qquad O \\ \qquad\quad /\!/ \quad\; \downarrow \qquad /\!/ \\ CH_3 - C - CH - C - OC_2H_5 \end{array}$$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac).	Diff. $\Delta\nu$
(2)d	19960	22938	2978
(3)d	19998	,,	2940
(2)	21188	,,	1750
(2)	21282	,,	1656
(2)	21488	,,	1450
(2)	21600	,,	1338
(6)	21731	24705	2974
(8)	21775	,,	2930
(0)	21829	,,	2876
(1)	22300	22938	638

$\Delta\nu$: 638, 1338, 1450, 1656, 1750, 2876, 2935, 2976.

TABLE III

Ethyl Malonate



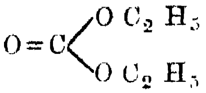
$$H \begin{array}{l} \nearrow O = C - O\,C_2H_5 \\ \qquad\quad\;\; | \\ \searrow H - C - C - OC_2H_5 \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad O \end{array}$$

(1)	19963	22938	2975
(1)	19999	,,	2939
(1)	21482	,,	1456
(8)d	21736	24705	2969
(4)d	21777	,,	2928
(00)	21830	,,	2875
(1)	24412	27389	2977
(1)	24453	,,	2936

$\Delta\nu$: 1456, 2875 2934, 2974.

TABLE IV.

Ethyl Carbonate



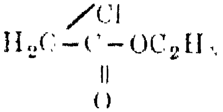
$O=C(OC_2H_5)_2$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. $\Delta\nu$
(1)	19964	22938	2974
(1)	19998	..	2940
(2)	21485	..	1453
(4)	21729	24705	2976
(5)	21773	,,	2932
(1)	21829	..	2876
(2)	23606	..	1099
(2)	23807	..	898
(2)	24411	27389	2978
(2)	21450	..	2939

$\Delta\nu$: 898, 1099, 1453, 2876, 2937, 2976.

TABLE V.

Ethyl Monochloroacetate



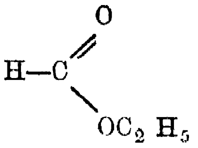
$H_2C(Cl)-C(=O)-OC_2H_5$

(2)	19962	22938	2976
(1)	19999	..	2939
(2)	21509	..	1429
(6)	21729	24705	2976
(7)	21771	..	2934
(1)	21825	..	2880
(2)	22059	22938	879
(2)	22148	..	790
(2)	23832	24705	873
(2)	23922	..	783
(2)	24412	27389	2977
(2)	24451	..	2938

$\Delta\nu$: 786, 876, 1429, 2880, 2937, 2976

TABLE VI.

Ethyl Formate,



$H{-}C({=}O){-}OC_2H_5$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. $\Delta\nu$
(1)	19963	22938	2975
(2)	19999	,,	2939
(2)	21221	,,	1717
(2)	21479	,,	1459
(2) d	21560	,,	1378
(5)	21733	24705	2972
(8)	21775	,,	2930
(1)	21827	,,	2878
(1)	21941	22938	997
(2)	22096	,,	842
(2)	23250	24705	1455
(2)	23330	,,	1375
(00)	23416	24516	1100
(00)	23516	,,	1000
(1)	23606	24705	1099
(1)	23703	,,	1002
(2)	23872	,,	833
(3)	24411	27389	2978
(3)	24450	,,	2938

$\Delta\nu$: 837, 1000, 1100, 1377, 1457, 1717, 2878, 2938, 2975.

TABLE VII.

Potassium and Ammonium Thiocyanates.

K – S – C≡N, NH$_4$ – S – C≡N

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. $\Delta\nu$
(12)	20871	22938	2067
(4)	22193	,,	745
(1)	22451	24516	2065
(10)	22641	24705	2064
(3)	23964	,,	741
(2)	2522	27290	2064
(2)	[illegible]	27854	2069
(3)	25324	27389	2065

$\Delta\nu$: 743, 2066.

TABLE VIII.

Phenyl Isothiocyanate $C_6H_5—N=C=S$.

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. Δν
(3)	15243	18308	3065
(2)	15676	17274	1598
(2)	15742	17337	1595
(5)	16714	18308	1594
(5)	19882	22938	3056
(6) band	20869	,,	2069
(10)	21346	,,	1592
(0)	21404	22995	1591
(3)	21449	22938	1489
(1)	21643	24705	3062
(10)	21695	22938	1243
(2)	21767	,,	1171
(4)	21934	,,	1004
(0)	22182	,,	756
(0)	22243	,,	695
(0)	22312	,,	626
(0)	22587	,,	351
(2) band	22640	24705	2065
(1)	22695	22938	243
(4)	23112	24705	1593
(1)	23212	,,	1493
(6)	23459	,,	1246
(1)	23536	,,	1169
(2)	23659	,,	1010

Δν : 243, 351, 626, 695, 756, 1007, 1170, 1245, 1491, 1594, 2067, 3061.

Cyanides and Cyanates

TABLE IX.

Potassium Cyanide K – C≡N.

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. Δν
(2)	20857	22938	2081
(½)	22103	,,	835
(2)	22626	24705	2 79
(½)	23867	,,	838
(0)	25209	27290	2081
(0)	25276	27354	2078
(½)	25309	27389	2080

Δν : 837, 2080.

TABLE X.

Double Cyanide of Potassium and Silver KAg (C≡N)$_2$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. Δν
(2)	20829	22938	2109
(½)	22079	,,	855
(2)	22600	24705	2105
(0)	25181	27290	2109
(0)	25245	27354	2109
(1)	25279	27389	2110

Δν : 855, 2109.

TABLE XI.

Potassium Cyanate K—O—C≡N.

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. Δν
(1)	20755	22938	2183
(0)	21624	,,	1314
(0)	21709	,,	1229
(1)	22100	,,	838

Δν: 838, 1229, 1314, 2183.

TABLE XII.

Acetonitrile $CH_3-C\equiv N$.

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. Δν
(2)	15359	18308	2949
(6)	19995	22938	2943
(6)	20681	,,	2257
(2)	21568	,,	1370
(1)	21705	,,	1233
(8)	21759	24705	2946
(2)	22016	22938	922
(½)	22260	24516	2256
(6)	22452	24705	2253
(1)	22559	22938	379
(2)	23330	24705	1375
(2)	23782	24705	923
(0)	24134	24516	382
(2)	24344	27290	2946
(3)	24407	27354	2947
(5)	24443	27389	2946
(2)	25035	27290	2255
(—) Hg	25093	27354	2261
(3)	25133	27389	2256

Δν : 380, 922, 1233, 1372. 2256, 2946.

TABLE XIII.

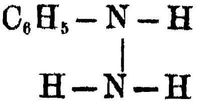
Aniline. $C_6H_5-NH_2$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. Δν
(1)	15244	18308	3064
(1)	16704	,,	1604
(1)	19580	22938	8358
(5)	19888	,,	3050
(8) br.	21338	22938 24705	1600 3367
(0)	21463	24516	3053
(10) br.	21657	22938 24705	1281 3048
(1)	21780	22938	1158
(2)	21910	,,	1028
(4)	21942	,,	996
(4) br.	22118	,,	820
(0)	22181	22995	814
(½)	22317	22938	621
(½)	22408	,,	530
(½)	22553	,,	385
(½)	22705	,,	233
(2)	23101	24705	1604
(1)	23432	,,	1273
(1)	23542	,,	1163
(2)	23678	,,	1027
(3)	23708	,,	997
(3)	23889	,,	816
(1)	24031	27389	3358
(0)	24165	24705	540
(0)	24327	24705 27389	378 3062

Δν : 233, 381, 536, 817, 997, 1028, 1160, 1277, 1603, 3055, 3361.

TABLE XIV.

Phenyl Hydrāzine



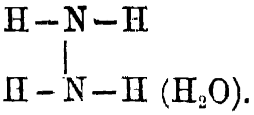
$$\begin{array}{c} C_6H_5-N-H \\ \quad\;\; | \\ \quad H-N-H \end{array}$$

Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. Δν
(1)	15249	18308	3059
(1)	16705	18308	1603
(4)	19889	22938	3048
(6) br.	21339	22938 24705	1599 3366
(0)	21465	24516	3051
(6)	21659	22938 24705	1279 3046
(1)	21780	22938	1158
(2)	21909	..	1029
(3)	21940	..	998
(3)	22120	..	818
(0)	22679	..	259
(0)	22505	..	433
(0)	22380	24705	2325
(00)	22180	22995	815
(2)	23099	24705	1606
(1)	23678	..	1027
(2)	23706	..	999
(2)	23892	..	813

Δν : 259, 433, 815, 999, 1028, 1158, 1279, 1603, 2325, 3051, 3366.

Table XV.

Hydrazine Hydrate



$$\begin{array}{c} H-N-H \\ | \\ H-N-H\ (H_2O). \end{array}$$

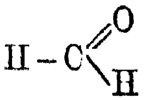
Int.	Wave no. of the Raman lines (Vac.)	Wave no. of the exciting lines (Vac.)	Diff. $\Delta\nu$
(2)	19663	22938	3275
(3)	21426	24705	3279
(1)	21490	,,	3215
(1)	21820	22938	1118
(1)	22032	,,	906
(0)	23595	24705	1110
(0)	23795	,,	910
(0)	24078	27354	3276
(1)	24112	27389	3277

$\Delta\nu$: 908, 1114, 3215, 3277.

Aldehydes.

Table XVI.

Formaldehyde

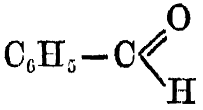


(1) diff.	21170	22938	1768
(1)	21477	,,	1461
(1) br.	21760	24705	2945
(0)	23666	,,	1039
(0)	23788	,,	917

$\Delta\nu$: 917, 1039, 1461, 1768, 2945.

TABLE XVII

Benzaldehyde



$C_6H_5-C(=O)H$

Int.	Wave no. of the Raman lines (Vac,)	Wave no, of the exciting lines (Vac,)	Diff. Δν.
(1)	15242	18308	3066
(1)	16606	,,	1702
(1)	16711	,,	1597
(3)	19872	22938	3066
(10)	21237	,,	1701
(0)	21290	22995	1705
(10)	21339	29938	1599
(1)	21445	22938 24516	1493 3071
(0)	21481	22938	1457
(1)	21546	,,	1392
(5)	21641	21705	3064
(6)	21731	22938	1207
(5)	21773	,,	1165
(1)	21914	,,	1024
(8)	21936	,,	1002
(4)	22108	,,	830
(0)	22186	,,	752
(1)	22285	,,	653
(3)	22323	,,	615
(4)	22499	,,	439
(1)	22709	,,	229
(2)	22814	24516	1702
(6)	23109	24705	1596
(0)	23209	,,	1496
(0)	23248	,,	1457
(1)	23313	24705 24516	1392 1203
(0)	23353	24516	1163
(4)	23502	24705	1203
(3)	23542	,,	1163
(0)	23684	,,	1021
(5)	23703	24705	1002
(1)	23880	,,	825
(00)	23947	,,	758
(0)	24054	,,	651
(1)	24090	,,	615
(1)	24271	,,	434
(0)	24474	,,	231

Δν . 230, 437, 615, 652, 755, 828, 1002, 1028, 1164, 1205, 1392, 1457, 1495. 1598, 1703. 065.

Raman Spectra of some Elements and simple Compounds.

BY

S. BHAGAVANTAM.

(*Received for publication, 23rd April, 1930*)

(Plate IV)

ABSTRACT.

The paper describes the results of a study of the Raman effect in certain simple molecules undertaken with a view to correlate them with their known molecular structures. Substances like chlorine, ammonia and sulphur dioxide, which are gases at ordinary temperature, have been liquified by cooling initially and the effect is studied at the room temperature with the liquids preserved in sealed tubes under pressure. The frequencies obtained in the various substances are as follows—chlorine : 556; diamond : 1333; phosphorous: 374, 468, 607; sulphur dioxide: 526, 1146, 1340; carbon disulphide: 655, 802; ammonia: 3216, 3304, 3380; chloroform: 263, 366, 668, 768, 1222, 1445, 3025; bromoform: 154, 222, 538, 654, 1146, 1437, 3023; phosphorous trichloride: 190, 260, 488, 512 ; arsenic trichloride : 159, 193, 370, 410; bismuth trichloride : 96, 242, 288 ; carbon tetrachloride: 217, 313, 459, 762, 792, 1537 ; silicon tetrachloride: 150, 221, 424, 614 ; titanium tetrachloride 120, 145, 382, 491 ; tin tetrachloride : 106, 131, 367 403. The scattered spectrum of SO_2 when compared with the analogous cases of CS_2 or CO_2 affords evidence in favour of a non-linear model for the SO_2 molecule. A close similarity exists between the Raman spectra of allied compounds such as chloroform and bromoform or the various trichlorides or tetrachlorides.

Introduction.

Since the discovery of the Raman effect, which has resulted in a new and a powerful weapon for a study of the molecular structure, several organic and inorganic substances have been studied by various investigators with a view to interpret their Raman spectra in terms of their constitution. It must however be remembered that from a theoretical point of view, relatively simple structures yield more interesting results. The simplest of the substances so far studied are the diatomic molecules namely H_2,O_2 and N_2. It is well known that a study of the effect in these cases has revealed transitions corresponding to changes in both vibrational and rotational quantum numbers and indicated the presence of the two kinds of hydrogen and apparently also two kinds of nitrogen. Recently Mclennan and his collaborators have succeeded in separating the two varieties of hydrogen and following their mutual transformation by the method of light scattering. These interesting results clearly show that such investigations extended to other relatively simple cases will be of great importance from the view point of theory. The present paper describes the results obtained by the author in the study of Raman spectra of certain simple molecules.

The simplest molecules are no doubt the polyatomic elements themselves and those of them in which there is a reasonable chance of observing the effect are carbon in the form of diamond, chlorine, phosphorous and sulphur. Of these the former three are studied by the author * in this paper. There are however other cases such as arsenic, antimony, etc., which could be studied in the vapour state or bromine, fluorine, etc., in the liquid or gaseous states, but the considerable experimental difficulties have prevented their investigation. A few polyatomic molecules like SO_2, NH_3, some trichlorides and tetrachlorides have also been chosen for the study and the results are described in this paper.[1] The choice has been restricted to such of the molecules as may be classified under one or other of the models represented by X_2, X_3, X_4, or AX_2, AX_8 and AX_4. A correlation of the observed results with the above molecular structures will be made from a dynamical point of view in another paper by the author. A glass two prism spectrograph of high light-gathering power supplied by Adam Hilger is used in the investigation.

---

* Diamond has been studied earlier by Mr. C. Ramaswamy whose results are being published elsewhere. Sulphur has been studied by Mr. Krishnamurti in this laboratory.

Experimental Results.

Chlorine.--This is the simplest of the substances studied. The gas is led off from the supply of a chlorine cylinder into a thick walled glass tube specially made to stand high pressures and is liquified by cooling it with liquid air. The liquid chlorine is then sealed off in the tube and is in equilibrium with its own vapour at the room temperature. It is coloured golden yellow and absorbs the blue and the violet rays of the mercury arc, transmitting only a portion of the green and yellow lines. Ilford panchromatic plates (H & D 2000) are used and three Raman lines could be clearly seen after an exposure of 13 days. The results are given in Table I

TABLE I. CHLORINE.

Exciting line A.U.	Raman lines.			$\Delta\nu$
	A. U.	I.	ν (vac)	
5460·7	5631·5	5	17752	556
5769·5	5959·8	3	16774	554
5790·5	5984·0	3	16707	558

$\Delta\nu$: 556.

It is interesting to note that as in the analogous cases of oxygen, nitrogen and hydrogen, the molecule as may be expected has only one vibrational frequency of a relatively low value in agreement with the greater mass of the constituent chlorine atoms. Just as in the above cases, Raman lines corresponding to pure rotational transitions may be expected, but the large moment of inertia of the molecule causes them to be much closer to the incident lines, and the dispersion of the instrument in the region investigated is not sufficient to resolve them. Similarly, the Raman line corresponding to the vibrational frequency ought also to have a structure due to an isotopic effect associated with the slightly different frequencies arising from $Cl_{35}Cl_{37}$, $Cl_{35}Cl_{35}$, and $Cl_{37}Cl_{37}$. Contrary to this however, the line does not show any, probably due to the lack of dispersion. The observed frequency 556 may be compared with 555[2] as revealed from the analysis of band spectra in the ultra-violet.

---

[1] Daure has studied some of the above compounds and the results obtained here are in good agreement with his results.

Diamond.—Carbon in the form of diamond may be described next. The scattered spectrum shows two intense and sharp Raman lines arising from one oscillation frequency combining with the mercury lines 1358 and 4046. The intensity with which the line comes out may be understood from the fact that the author has been able to get very good photographs showing the line prominently in one hour with tiny diamonds. In addition to this frequency the scattered light consists of a prominent continuous spectrum, the significance of which will be discussed in another paper.

TABLE II. DIAMOND.

Exciting line A.U.	Raman lines.			$\Delta\nu$
	A. U.	I.	ν (vac)	
4046·6	4277·0	10s	23374	1331
4358·3	4627·5	10s	21604	1334

$\Delta\nu$: 1333

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[2] Handbuch Der Physik, Vol. 21, p. 547.

Phosphorous.—The scattered spectrum of yellow phosphorous immersed in water in the solid state is photographed and is found to contain several Raman lines, all excited by the green and the yellow rays of the mercury arc as the substance is very nearly opaque to the blue and the violet region of the spectrum. It is a tetratomic molecule and the distribution of the frequencies conforms to a tetrahedral model in agreement with the fact that it belongs to the cubic system of crystals. The results are given in table III.

TABLE III. YELLOW PHOSPHOROUS.

Exciting line.	Raman lines.			$\Delta\nu$	Exciting line.	Raman lines.			$\Delta\nu$
A. U.	A. U.	I	ν (vac)		A. U.	A. U	I	ν (vac)	
5460·7	5574·4	1	17934	374	5769·5	5929·5	1	16860	468
,,	5604·3	3	17839	469	5790·5	5951·9	1	16797	468
,,	5648·8	6	17698	610	5769·5	5978·8	2	16721	607
					5790·5	6000·2	2	16662	608

$\Delta\nu$: 374, 468, 607.

Sulphur dioxide.—Sulphur dioxide is led off from a cylinder and liquified in a thick walled glass tube by cooling and sealed off. The scattered spectrum is photographed at the room temperature. Results are given in table IV.

TABLE IV. SULPHUR DIOXIDE.

Exciting line.	Raman lines.			$\Delta\nu$	Exciting line.	Raman lines.			$\Delta\nu$
A. U.	A. U.	I	ν (vac)		A. U.	A. U.	I	ν (vac)	
4358·3	4628·3	0d	21598	1340	4077·7	4277·8	2s	23370	1146
,,	4587·4	10s	21793	1145	4046·6	4243·4	10s	23559	1146
,,	4460·6	0d	22412	526					

$\Delta\nu$: 526, 1146, 1340.

It is interesting to note that the two analogous cases of CS_2 (Table V) and CO_2[3] also give very similiar results in that they show an intense Raman line in about the same position as the *1146 of* SO_2 *with a relatively feebler component on its longer wave length side.* In addition to this however a Raman line occurs at $\Delta\nu$ 526 in SO_2, the analogue of which is not present in either CO_2 or CS_2, a result which is evidently connected with the fact that the molecule of SO_2 is a triangular model whereas CO_2 and CS_2 are linear. The principal line in SO_2 is remarkably sharp and strong when compared to the other feebler lines present on its either side which are extremely diffuse. The significance of this result is not very clear, but the author is of the opinion that it is in some way connected with the polarity of the molecule. The connection between association and the spectral character of the Raman lines will be discussed in greater detail in another paper.

Carbon disulphide.—Raman effect in this liquid is studied and the results are given in table V.

TABLE V. CARBON DISULPHIDE.

Exciting line.	Raman lines.			$\Delta\nu$	Exciting line.	Raman lines.			$\Delta\nu$
A. U.	A. U.	I	ν (vac)		A. U.	A. U.	I	ν (vac)	
4358·3	4515·7	2	22139	799	4077·7	4189·7	0	23861	655
,,	4486·3	10	22284	654	4046·6	4183·0	1	23900	805
4347·5	4475·3	0	22339	656	,,	4157·1	10	24048	657
4358·3	4238·6	0	23586	648					

$\Delta\nu$: 655, 802.

Ammonia.—As before, the gas is liquified by cooling and the liquid is collected into a thick walled glass tube which is then sealed off. The results are given in table VI.

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[3] Phys. Rev., Vol. 34, p. 582 (1928).

TABLE VI. AMMONIA.

Exciting line.	Raman lines.				Exciting line.	Raman lines.			
A. U.	A. U.	I	ν (vac)	$\Delta\nu$	A. U.	A. U.	I	ν (vac)	$\Delta\nu$
4358·3	5111·6	0	19558	3380	3663·3	4183·5	0d	23897	3393
,,	5089·4	4d	19643	3295	,,	4167·8	5d	23987	3303
,,	5068·7	2d	19723	3215	3654·8	4157·0	2	24049	3305
4077·7	4712·9	2d	21212	3304	3650·1 3663·4	4151·3	6b	24082	3307 3208
,,	4693·1	2d	21302	3211					
4046·6	4671·2	6	21402	3303	3650·1	4136·0	3	24171	3218
,,	4652·4	4	21488	3217					

ν: 3216, 3304, 3380.

A diffuse band corresponding to a shift of 1070 wave numbers could be seen clearly on the plate but could not be measured accurately. Daure has however reported another band shifted by 1580, which happens to fall on the group of 3 lines excited by 4046 and hence its presence could not be decided with certainity in the author's plate.

TABLE VII. CHLOROFORM.

Exciting line.	Raman line			$\Delta\nu$	Exciting line.	Raman lines.			$\Delta\nu$
A. U.	A. U.	I	ν (vac)		A. U.	A. U.	I	ν (vac)	
4358·3	4651·3	0	21493	1445	4358·3	4108·9	4	22675	263
4046·6	4610·5	3	21684	3021	,,	4309·6	1	23198	−260
4358·3	4603·6	0	21716	1222	,,	4290·8	1	23299	−361
,,	4509·3	1d	22170	768	4046·6	4159·3	3	24036	669
,,	4489·0	5	22270	668	3650·1	4103·9	1	24360	3029
,,	4429·1	5	22572	366	4046·6	4090·1	2	24442	263

$\Delta\nu$; 263, 366, 668, 768, 1222, 1445, 3025.

TABLE VIII. BROMOFORM.

Exciting line.	Raman lines.			$\Delta\nu$	Exciting line.	Raman lines,			$\Delta\nu$
A. U.	A. U.	I	ν (vac)		A. U.	A. U.	I	ν (vac)	
4358·3	4649·5	0	21501	1437	4046·6	4243·3	1	23560	1145
4046·6	4610·1	6	21685	3020	4077·7	4170·2	0	23973	543
4358·3	4587·6	2	21792	1146	4046·6	4156·9	4b	24050	655
,,	4486·3	6b	22284	654	4077·7	4115·1	1	24294	222
,,	4463·0	8	22400	538	3650·1	4103·5	3	24363	3026
,	4400·9	10	22716	222	4046·6	4083·2	6	24484	221
,,	4387·8	10	22784	154	,,	4072·0	6	24551	154
,,	4329·3	6	23092	−154	,,	4021·6	4	24859	−154
..	4316·4	6	23161	−223	,,	4010·4	4	24928	−223
,,	4258·7	2	23475	−537	...	...	...	...	...

$\Delta\nu$: 154, 222, 538, 654, 1146, 1437, 3023.

The close similarity between the Raman spectra of the above two compounds, chloroform and bromoform, is remarkable in that there is an exact one-to-one correspondence of the Raman frequencies. From a comparison of the data in these two liquids it is clear that the Raman lines given by $\Delta\nu$ 263, 366, 668, 768 and 1222 in $CH\,Cl_3$ are analogous to those represented by $\Delta\nu$ 154, 222, 538, 654 and 1146 in $CHBr_3$, the smaller shifts in the latter being evidently due to the fact that the bromine atom is heavier than the chlorine. The other two frequencies 1445 and 3025 which have practically the same values in both the liquids are evidently due to oscillations in which carbon and hydrogen alone are taking part.

The trichlorides of phosphorous, arsenic, and bismuth have been studied, the former two in the liquid state and the third dissolved in aqueous hydrochloric acid. The results are given in tables IX, X and XI respectively. In these and the tetrachlorides Daure has given the frequencies correct to the second digit, whereas the author's values are a little more precise in that they are correct to a few units in the third.

TABLE IX. PCl_3.

Exciting line A. U.	Raman lines.			$\Delta\nu$	Exciting line A.U.	Raman lines.			$\Delta\nu$
	A.U.	I	ν (vac)			A.U.	I	ν (vac)	
4358·3	4457·8	10	22426	512	4358·3	4309·6	1	23198	—260
,,	4452·9	2	22451	487	4046·6	4132·1	8	24194	511
,,	4408·2	10	22679	259	,,	4128·3	2	24216	489
,,	4394·8	10	22748	190	,,	4089·6	2	24445	260
,,	4322·8	2	23127	—189	,,	4016·2	0	24892	−187

$\Delta\nu$: **190, 260, 488, 512.**

TABLE X. $AsCl_3$.

Exciting line A.U.	Raman lines.			$\Delta\nu$	Exciting line A.U.	Raman lines.			$\Delta\nu$
	A.U.	I	ν (vac)			A.U.	I	ν (vac)	
4358·3	4437.7	10	22528	410	4358·3	4282·7	4	23343	−405
,,	4430·1	6b	22567	371	4077·7	4147·2	2	24106	410
,,	4395·3	6	22745	193	4046·6	4114·8	10	24296	409
,,	4388·7	8	22779	159	,,	4072·6	6	24547	158
,,	4328·4	5	23097	−159	,,	4021·4	4	24860	−155
,,	4322·4	4	23130	−192	,,	4015·9	2	24894	−189
,,	4289·4	2b	23307	−369	...	...	...	...	...

$\Delta\nu$: **159, 193, 370, 410.**

TABLE XI. $BiCl_3$.

Exciting line A.U.	Raman lines.			$\Delta\nu$
	A.U.	I	ν (vac)	
4358·3	4413·7	10b	22650	288
,,	4401·8	2b	22696	242
,,	4376·6	8b	22842	96*

$\Delta\nu$: 96, 242, 288.

It will be seen that they all give four fundamental frequencies with the exception of bismuth in which two of them presumably join up resulting in a broad band. The fourth frequency always comes out with a relatively greater intensity. Such a close similarity between their Raman spectra, not only in the number of frequencies but also in their intensity relationships, is in agreement with their allied structures and suggests that they are all characteristic oscillations of a molecular model like AX_3 in general. It will be seen that the oscillation frequencies become smaller and smaller as we go from phosphorous to arsenic to bismuth as might be expected, since the vibrating system is being loaded with atoms of increasing weight. The broad bands which occur in a solution of bismuth chloride as contrasted with the sharp lines of the chlorides of phosphorous and arsenic may be associated with the fact that a portion of the molecules are in an ionised condition. It is interesting to notice that with increasing atomic weight, the interval between the third and the fourth Raman frequencies goes on increasing, whereas that between the first and the second goes on decreasing. In fact in the trichloride of phosphorous, the lightest of the three the third and the fourth frequencies are so close that they can only be separated with good dispersion. On the other hand, the first and the second in the heaviest, *viz.*, bismuth trichloride, have given place to one unresolved broad band.

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* The centre of a broad brand is measured.

The tetrachlorides of carbon, silicon, titanium and tin have also been studied. The results are given in tables XII, XIII, XIV and XV respectively. Carbon tetrachloride has been studied by various investigators. The tetrachloride of tin has been studied by Petrikaln and Hochberg and their results are in fair agreement with those of the author.

TABLE XII. CCl_4.

Exciting line A.U.	Raman lines.			$\Delta\nu$	Exciting line A.U.	Raman lines.			$\Delta\nu$
	A.U.	I	ν(vac)			A .U.	I	ν (vac)	
4358·3	4671·4	2d	21401	1537	4358·3	4272·5	5	23399	−461
,,	4514·9	6	22143	795	4016·6	4180·4	4	23915	790
,,	4508·4	6	22175	763	,,	4175·0	4	23945	760
,,	4447·5	10	22178	460	4077·7	4155·3	3	24059	457
4347·5	4437·0	2	22531	464	,,	4130·4	2	24204	312
4339·2	4428·5	1	22575	,,	4016·6	4123·0	10	24247	458
4358·3	4419·1	8	22623	315	4077·7	4114·5	1	24297	219
4347·5	4408·2	1	22679	316	4016·6	4098·3	6	24394	311
4358·3	4399·7	8	22722	216	,,	4082·5	5	24488	217
4347·5	4389·9	1	22773	222	,,	4011·0	4	24924	−219
4358·3	4317·1	6	23157	−219	,,	3996·1	3	25017	−312
,,	4299·3	6	23253	−315	,,	3972·4	2	25167	−462

$\Delta\nu$: 217, 313, 459,* 762, 792, 1537.

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* The structure of the Raman lines characterised by this frequency is peculiar in that they have an extremely sharp edge on the long wave length side, the intensity rapidly falling off towards the short wave lengths. The phenomenon is very marked in the well exposed Stokes lines.

TABLE XIII. $SiCl_4$.

Exciting line A.U.	Raman lines.			$\Delta\nu$	Exciting line A.U.	Ramam lines.			$\Delta\nu$
	A.U.	I	ν(vac)			A.U.	I	ν(vac)	
4358·3	4478·1	1d	22325	613	4358·3	4316·7	2	23159	−221
,,	4440·2	10s	22515	423	,,	4279·2	3	23362	−424
,,	4400·8	5	22717	221	4046·6	4149·9	1d	24000	615
,,	4387·1	5	22788	150	,,	4117·4	8s	24280	426
,,	4330·3	3	23087	−149	,,	4071·9	2	24552	153

$\Delta\nu$: 150, 221, 424, 614.

TABLE XIV. $TiCl_4$.

Exciting line A.U.	Raman lines.			$\Delta\nu$	Exciting line. A.U.	Raman lines.			$\Delta\nu$
	A.U.	I	ν (vac)			A.U.	I	ν(vac)	
4358·3	4454·3	0	22441	494	4358·3	4286·2	1	23323	−380
,,	4432·1	6	22556	382	4046·6	4066·0	4	24587	118
,,	4386·1	0	22793	145	,,	4027·1	3	24825	−120
,,	4381·4	4	22817	121	...	...	...	...	...

$\Delta\nu$: 120, 145, 382, 494.

TABLE XV. $SnCl_4$.

Exciting line A.U.	Raman lines.			$\Delta\nu$	Exciting line A.U.	Raman lines.			Δ
	A.U.	I	ν(vac)			A.U.	1	ν (vac)	
4358·3	4436·3	6	22535	403	4353·3	4289·8	6	23305	−367
,,	4429·2	10	22571	367	,,	4285·0	2	23331	−393
4347·5	4418·2	2	22627	368	4046·6	4068·3	6	24573	132
4339·2	4410·8	1	22665	374	,,	4064·2	5	24598	107
4358·3	4383·4	6	22807	131	,,	4029·8	4	24808	−103
,,	4378·6	5	22832	106	,,	4026·1	4	24831	−126
,,	4334·2	3	23066	−128	,,	3987·5	3	25071	−366

$\Delta\nu$: 106, 131, 367, 403.

The same phenomenon as noticed in the trichlorides, namely a close resemblance between their Raman spectra, may also be seen clearly in the series of tetrachlorides. All the substances show four principal Raman frequencies, the third one being the most prominent in every case. The case of carbon tetrachloride however offers an exception in that the fourth-frequency has split into two close frequencies of about the same intensity. In addition to this splitting, a new frequency of about 1,500 appears in its scattered spectrum. This is rather diffuse and its presence is difficult to understand. Such a departure in the case of CCl_4 from the general model of a tetrachloride is presumably connected with the fact that the carbon atom is slightly anisotropic and as a result the chlorine atoms are not arranged on the corners of a perfect tetrahedron.

In conclusion, the author desires to express his best thanks to Prof. Sir C. V. Raman for his kind encouragement and keen interest in the entire work. All the problems have been taken up at his suggestion.

4

Influence of Polymerisation and Molecular Association on the Raman Effect.

BY

S. BHAGAVANTAM.

(*Received for publication, 23rd April, 1930*)

(Plate IV)

Abstract.

The phenomenon of polymerisation has been investigated by the method of light scattering in the typical case of sulphur trioxide. At ordinary temperatures this substance is a mixture of S_2O_6 and SO_3, the Raman spectrum consisting of frequencies 290, 370, 535, 666, 697, 1068, 1271, 1403, 1489 arising from the two different molecules. With rise of temperature, the molecules of S_2O_6 split into those of SO_3 resulting in the disappearance or weakening of the Raman lines corresponding to 290, 370, 666, 697, 1271, 1489 which are therefore attributable to S_2O_6. The others, *viz.*, 535, 1068 and 1403 correspondingly brighten up and are attributed to SO_3. On cooling all the lines resume their original intensities and the phenomenon is thus perfectly reproducible.

The effect of molecular association on the Raman spectra is discussed with special reference to ammonia studied by the author. The frequency 3333·6 given by gaseous ammonia is represented by three rather broad lines in the liquid at the room temperature at 3216, 3304 and 3380, their relative intensities being 2, 4, 0. This result taken together with that of Daure who finds that the three components are all of comparable intensity at much lower temperatures, suggests that the outer two components are due to association and hence show a weakening with rise of temperature. Another diffuse Raman line corresponding to 1070 wave numbers shows no such alteration in intensity and is therefore presumably due to unassociated molecules. The cases of other polar molecules such as H_2O, SO_2, HCl and HBr are briefly reviewed. Such diminution in intensity with rise of

temperature is also noticeable in the 3·13μ band of water. Sulphur dioxide shows, in addition to a sharp line, two remarkably broad and diffuse Raman lines. The frequencies of some of the above polar molecules as determined in the gaseous and liquid states differ from each other to an appreciable extent. The significance of such a result is not quite clear but the polarity and the consequent association in the liquid may in part be responsible.

1. *Introduction.*

A study of the Raman Effect has now come to be recognised and extensively used as a means of elucidating the various problems connected with molecular structure and it is evidently of great interest to follow up the various physical and chemical processes through such investigations. The transformation of β-hydrogen to α-hydrogen at low temperatures has, for instance, been demonstrated by Mclennan and his collaborators by the method of light-scattering.[1] An altogether different kind of change is encountered in the case of electrolytes which break up into their constituent ions in solution the extent of dissociation depending on the dilution. That such a process of ionisation could be followed up by means of light scattering has recently been shown by I. R. Rao [2] in the case of the nitric acid molecules. It is evident that further studies on the lines indicated by him will lead to interesting results in connection with the theories of electrolysis. In the course of a study of the Raman spectra of certain simple compounds, the author has come across two other interesting cases in sulphur trioxide and ammonia whose study throws light on the phenomena of polymerisation and molecular association. In this paper it is proposed to discuss the results obtained in these two cases in detail and consider the influence of the above phenomena on Raman spectra in general making use of the available evidence.

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[1] Trans. Roy. Soc. Canada, Vol. 23, Part II, Sec. III, p. 247 (1929).

[2] I. R. Rao, Nature, Vol. 124, p. 762 (1929).

2. *Experimental results and discussion.*

Sulphur trioxide:—An unopened bulb containing sulphur trioxide in the form of a silky fibrous solid supplied for analytical purposes is made use of in the investigation. The substance melts when kept for a considerable length of time in boiling water and subsequently remains liquid even at room temperature. A large two prism glass spectrograph of high light gathering power constructed by Adam Hilger is used and two spectrograms of the scattered light, one with the liquid at the room temperature (30° C) and another at a higher temperature[1] are photographed side by side under practically identical conditions of illumination. The results are given in table I. A horizontal line in the intensity column indicates that the line is not visible at all.

TABLE I, Sulphur trioxide.

Exciting line A.U.	Raman lines.				$\Delta\nu$
	A.U.	Intensity.		ν (Vac.)	
		Cold	Hot.		
4358 3	4661·3	0*d*	—	21447	1491
,,	4642·7	1*b*	4*b*	21533	1405
,,	4614·2	7	1	21666	1272
,,	4571·3	6	10	21870	1068
,,	4495·1	1	—	22240	698
,,	4489·1	1	—	22270	668
,,	4462·3	2	4	22404	534
,,	4429·8	6	1	22568	370
,,	4414·1	4	0	22648	290
4046·6	4305·6	1*d*	0	23219	1486
,,	4290·1	1*b*	3*b*	23303	1402
,,	4265·9	6	1	23435	1270
,,	4229·5	6	10	23637	1068
,,	4163·9	1	—	24009	696
,,	4158·4	1	—	24041	664
,,	4136·1	1	3	24170	535
,,	4094·6	4	0	24416	289

$\Delta\nu$ S_2O_6: 290, 370, 666, 697, 1271, 1489.

SO_3: 535, 1068, 1403.

A mean temperature of about 95°C is maintained by keeping the bulb in a hot air bath.

The striking fact that emerges from the above table is that the mutual intensity relationships of the different Raman lines show considerable variations with temperature, some of them tending to disappear altogether at higher temperatures and the others becoming correspondingly brighter. It may be inferred that if the temperature interval is sufficient, the entire Raman spectrum would change and give place to altogether new frequencies. Chemical evidence shows the presence of two varieties of SO_3 having distinctly different melting points one consisting of polymerised molecules with the formula S_2O_6 at lower temperatures which gradually passes into the other variety if kept at a temperature between 50°C and 100°C having a lower molecular weight corresponding to SO_3.[1] The Raman spectrum at the room temperature consists of no less than nine frequencies whereas on heating six of them, *viz.*, 290, 370, 666, 697, 1271 and 1489, definitely weaken the other three brightening up. Thus here we have a a case of dissociation represented by $S_2O_6 \longrightarrow 2\,SO_3$, the former being a definite chemical molecule and hence giving its own characteristic Raman spectrum distinct from that of SO_3. The lines arising from the frequencies 535, 1068, 1403 are due to SO_3 and are also present at the room temperature, though feebly, because at such temperatures the system presumably attains a certain equilibrium ratio. SO_3 may be compared with the general system of the AX_3 type and by analogy may be expected to show four different frequencies.[2] In some cases however it happens that two of them are very close and give rise to a broad band. In agreement with the same we have here two sharp Raman lines and one broad band which is probably an unresolved doublet. The lines due to S_2O_6 however reappear on cooling the bulb, regaining their original intensity, and thus the phenomenon is perfectly reproducible and the dissociation or the recombination can be followed up through the various stages by studying the Raman spectra through the necessary range of temperatures.

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[1] Modern Inorganic Chemistry, J. W. Mellor, p. 428 (1916).

[2] This and the subsequent references are to author's papers in this volume.

A similar case of polymerisation may be seen in acetaldehyde and paraldehyde.[1] Frequencies 521, 688, 780, 905, 1137, 1270, 1417, 1727, 2850, 2922, 2997 appear in the Raman spectrum of the former whereas that of the latter shows 472, 525, 735, 776, 840, 900, 962, 1025, 1105, 1178, 1350, 1455, 2850, 2945, 3000. Except the frequencies in the neighbourhood of 3.3μ which are known to arise from C-H linkages, there is not much that is common between them. This again is a case where three of the acetaldehyde molecules have actually joined up in the course of polymerisation resulting in a distinctly different structure.

Ammonia :—The detailed analysis of its Raman spectrum is given by the author in another paper. It reveals three prominent frequencies 3216, 3304 and 3380. Besides these there is another relatively weak and diffuse line shifted by about 1070 wave numbers from λ 4358. One other weak line corresponding to 1580 has been reported by Daure but its presence could not be definitely confirmed in the author's plates as it falls within the 3μ group of lines excited by λ4046. From the photographs reproduced by Daure[2] one gets the impression that the three lines given by 3216, 3304 and 3380 are more or less of the same intensity. The author's results are however quite different in that on his plate the average ratio of their intensities is 2 : 4 : 0. The Raman line corresponding to 3380 is relatively so feeble that of the group of lines excited by λ4358, the one characterised by this frequency is hardly visible whereas the other two are very well exposed. There does not however seem to be any such alteration in the intensity of the diffuse line corresponding to 1070 wave numbers. Such a result is significant, if we remember that Daure's photographs were taken at a much lower temperature, (*i. e.*) below the boiling point of ammonia with the liquid at atmospheric pressure, whereas the author worked at the room temperature (about 30°C) with liquid ammonia sealed and preserved in glass tubes. Such a relative weakening of the component lines with rise of temperature is a strong evidence in support of the view that they are due to some kind of association, because one might expect the molecules to be associated to a much less extent at the higher than at the lower temperatures.

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[1] Venkateswaran & Bhagavantam; "Raman spectra of some aldehydes and mesitylene," Proc. Roy. Soc. (under publication).

[2] Mol. spectra and mol. structure, Faraday Society, p. 825 (1929).

The author's intensity relationships as compared with those published by Daure clearly suggest that, if the spectrum is photographed at still higher temperatures, the components would almost disappear leaving the principal central line alone to be present. The results obtained by Dickinson, Dillon and Rasetti[1] with gaseous ammonia are in entire agreement with the above, in that they have been able to record only one vibrational frequency of 3333·6 which is presumably represented by the central line in the liquid given by 3304. Recently however, it was suggested by Austin[2] that the components are due to a kind of secondary Raman effect arising from the combination of a relatively low frequency of 80 with the principal frequency thus giving rise to the Raman lines 3300 ± 80, such a frequency presumably arising in a losely associated molecule $H_3N{-}NH_3$. The above intensity relationships observed by the author, namely, the extreme feebleness of $3300 - 80$ as compared with $3300 + 80$, definitely exclude such a possibility. To decide this point with greater certainty, the author has studied the polarisation characters of these lines. The one arising from 3380 is very imperfectly polarised whereas the one given by 3216 is very well polarised. Such widely different degrees of polarisation are in entire disagreement with the origin suggested above for them. In all probability they represent only the principal frequency modified by association in the liquid. The appearance of the two new frequencies, *viz.*, 1070 and 1580 in the liquid has recently been explained as due to a new molecule $(NH_3)_2$[1] but the present author is of the opinion that they really represent the characteristic oscillations of the NH_3 molecule itself, a view which finds support in the fact that we are forced to accept them (6·1 and 10·55μ)[2] as fundamental frequencies in the interpretation of the infra-red absorption of ammonia. Further if they are due to associated molecules, as the two outer components of the 3μ group of lines are, then one would expect them to show a similar weakening or disappearance with rise of temperature. In fact the Raman line corresponding to 3380 is very intense in Daure's photograph and could be only faintly seen on the author's whereas the one shifted by 1070 wave numbers is only just visible in his picture and could be seen quite as easily in the author's. This persistence is connected with the fact that it is a fundamental characteristic of the unassociated molecule although it is relatively a very feeble one, a fact which might account for its presumed absence in the gaseous state.

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[1] Phyl. Rev., Vol. 34, p. 582 (1929).

[2] Nature, Vol. 125, p. 464 (1930).

One other interesting feature which may be mentioned here is the difference between the frequency 3333·6 given by gaseous ammonia and 3304 corresponding to the principal line in the liquid. Analogous differences in other polar compounds will be mentioned later but the evidence is too scanty to decide if such a phenomenon is in any way connected with polarity and the consequent association.

Sulphur dioxide :—The molecule of SO_2 is known to be polar and hence there is bound to be some kind of association in the liquid state. The only evidence in favour of the above from light scattering is that liquid SO_2 at the room temperature in addition to a sharp line, gives two remarkably diffuse and broad Raman lines. It must however be remembered that the spectrum is not in any way more complicated than what we might expect for an individual molecule like SO_2.

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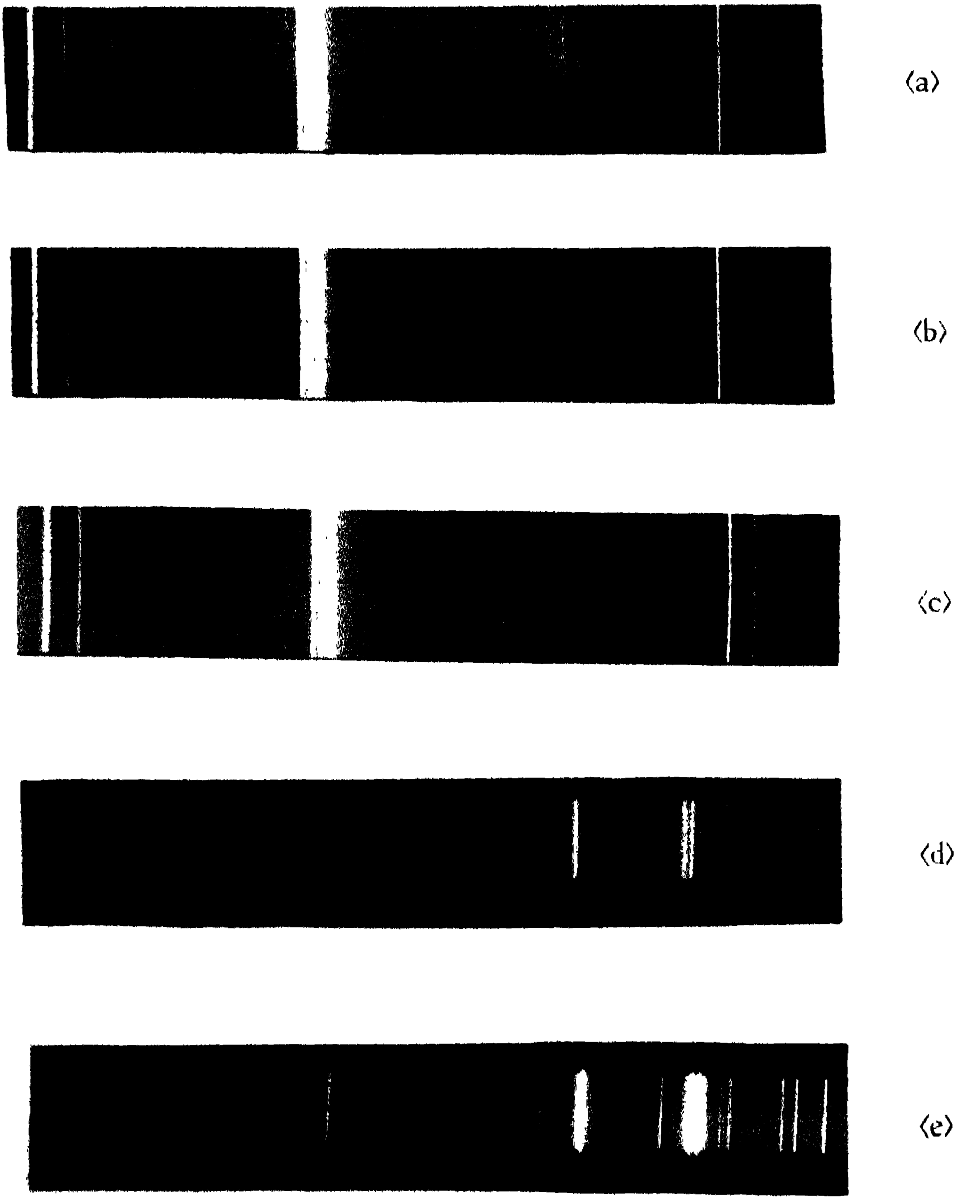
[1] Dadieu & Kohlrausch, Naturwiss, Vol. 18, p. 154 (1930).

[2] Robertson & Fox, Proc. Roy. Soc., Vol. 120, p. 207 (1928); see also J. W. Ellis, Jour. Frank. Inst., Vol. 208, p. 507 (1929).

Water :—Another interesting case of association is presented by water which has been investigated by various workers with a view to elucidate the problem of its constitution. The results obtained are of exceptional interest in that the Raman spectrum shows only one weak and broad band extending over several Angstrom units. There are however certain differences of opinion regarding the structure of this band in that various investigators have recognised it as only a double band, contrary to which Venkateswaran and Ganesan have recorded that the band consists of three components gradually shading into one another, their infra-red wave lengths being 2·77, 2·90, 3·13μ. In view of this their plates have been re-examined by the author who finds that the band has a distinct triplet structure, such a structure being clearly seen on the plate intended to show the effect of temperature because the three components seem to be influenced to different extents. The component corresponding to 3·13μ can hardly be seen in the spectrogram taken at 80°C, whereas the others show very little variation in intensity, a result which no doubt suggests that it is a different oscillation frequency arising in the complexes of the type $(H_2O)_n$. But a breaking up of such complexes at higher temperatures should result in a corresponding increase of the intensity of the other components and no such observation has however been recorded by them. On the contrary they show if any, only a slight diminution. The case is in many respects analogous to that of ammonia and the author is inclined to explain the components as merely modified forms of the principal frequency itself at 2·9μ characteristic of the H_2O molecule. It is of great interest here to compare the values of

Raman Spectra.



(a) Ammonia polarisation ; (b) Sulphur trioxide polarisation ,
(c) Sulphur trioxide temperature effect ,
(d) Chlorine ; (e) Phosphorus

the oscillation frequencies in the liquid and the vapour states. Investigations on the infra-red spectrum of water vapour reveal absorption bands at 1600, 3735 and 3850 which may be compared with 3200, 3453 and 3610. The differences are even more striking than in the case of ammonia.

Such a change in the principal frequency itself is also noticed in other polar compounds especially HCl and HBr which in the gaseous state show frequencies 2886 and 2559 as revealed in the infra-red absorption spectra whereas Raman transitions in these liquids are caused by frequencies 2781 and 2479 respectively. Contrary to such cases, non-polar molecules like CH_4 show, if at all, only inappreciable differences (2914 for the gas and 2908 for the liquid). If such a coincidence has any real significance is more than what we can say from the available evidence. Recently however, Salant and Sandow have attempted to correlate this change with the Lorentz polarisation field and Dennison's 'effective charge.' In this connection, more detailed studies of the various simple polar molecules in the gaseous and liquid states is of great interest and the author hopes to undertake the same at a latter date.

In conclusion, the author takes this opportunity of expressing his thanks to Prof. Sir C. V. Raman for his kind encouragement and interest in the work.

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[1] Nisi has independently recorded a triplet structure in a recent paper, Jap. Jour. Phys., Vol. 5, p. 119 (1929).

[2] Salant and Sandow, Phys. Rev., Vol. 35, p. 215 (1930),

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Polarisation of the Lines in Raman Spectra.

By

S. BHAGAVANTAM.

(Received for publication, 26th April, 1930.)

(Plate V.)

ABSTRACT.

A systematic study is made of the state of polarisation of the various Raman lines occurring in some simple compounds, *viz.*, SO_2, CS_2, SO_3, NH_3, $CHCl_3$, $CHBr_3$, trichlorides of phosphorous, arsenic and bismuth and the tetrachlorides of carbon, silicon, titanium and tin. Close similarities are shown to exist between the polarisation characters of the Raman spectra arising from compounds having analogous structures. It is suggested that the geometry of the various oscillations is one of the chief factors which influence the polarisation of a Raman line. The depolarisation factor generally ranges from 0 to 1. Contrary to this however, in the case of SO_3, a Raman line shifted by 1403 wave numbers is found to have a depolarisation greater than unity. The significance of this result is not clear. A high degree of polarisation for any Raman line is generally accompanied by relatively large intensity but the converse relation is not true. Existing explanations for the polarisation phenomena in Raman spectra are briefly reviewed.

1. *Introduction.*

It has been pointed out by Sir C. V. Raman, in his first report of the discovery[1] that some of the modified lines appearing in the scattered spectra are strongly polarised. In subsequent papers[2] the principal features regarding their state of polarisation have also been indicated. It need not be emphasised here that a more detailed and systematic study of their polarisation characters is a matter of great importance *from a theoretical point of view. The question of intensity of the various Raman lines, the mutual relationship of the* classical and the quantum scattering, the mechanism of the new phenomenon and various other fundamental problems are intimately related to that of polarisation. The subject has in the past received attention from Pringsheim, Cabannes, Daure and others. The close similarity that is usually observed between the Raman spectra of compounds having related structures is a fact of great significance recently brought out in a most striking manner in the cases of the various trichlorides and the tetrachlorides.[3] It is obviously of great interest to pursue such studies in various groups marked by simplicity of structure and extend them to other characters, in particular those of intensity and polarisation. Such results have been reported, especially by Cabannes,[4] but the information available is very meagre and hence the author has made a systematic study of the polarisation characters of the different Raman lines in the above series of trichlorides and tetrachlorides and in various other simple compounds, *viz.*, SO_2, SO_3, CS_2, $CHCl_3$, $CHBr_3$ and NH_3. The present paper consists of a description of the above results with a brief discussion of the same.

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[1] Ind. Jour. Phys., Vol. 2, p. 387 (1928).

2. *Experimental.*

A large two prism glass spectrograph of high light gathering power made by Adam Hilger is made use of in the investigation. The light of a mercury lamp is focussed by a powerful condenser to the centre of the liquid under investigation contained in a suitable vessel, so arranged that the slit of the spectrograph is situated just far enough from it to allow the interposition of a large nicol. No lens is used for recondensing the scattered light on to the slit of the spectrograph. In most cases, the liquids purchased in the market have been purified by distillation in evacuated double bulbs. In some cases however, they have been used as such for convenience. Sulphur dioxide and ammonia are studied at the room temperature the liquids being preserved under pressure in sealed tubes.

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[2] Proc. Roy. Soc., Vol. 122, p. 23 (1929).

[3] P. Daure, Compt. Rend., Vol. 187, p. 940 (1928).

[4] Mol. Spectra and Mol. Structure, Faraday Society Report, p. 813 (1929).

Two spectrograms are always taken side by side on the same negative, one with the vibration direction of the nicol parallel to the track of light in the liquid and the other perpendicular, the conditions of illumination being identical in both cases. A difficulty however arises in the evaluation of the polarisation values especially if the exposures in the two cases are also identical. It is known from Fresnel's equations that after transmission through the boundary of any medium, the component polarised in the plane of incidence loses more than the one polarised normal to the plane of incidence and hence it must be inferred that the ratio of the intensities of the two components in the scattered light, a measure of the depolarisation in our case, is no longer the same before and after transmission through the spectrograph. The magnitude of the effect depends on the number of surfaces involved and on the obliquity of incidence on each surface. In consequence of the latter fact a slight dependence on the wave length may also be expected. It is therefore essential to calibrate the instrument in the range under investigation and suitably compensate for the same in the photometric evaluation of the polarisation. The slit is illuminated strongly by the direct light of a mercury lamp and the state of polarisation of each line determined visually by using a double image prism and a nicol suitably mounted on a graduated circle. Independent determination is also made by the photographic method, by interposing a nicol in front of the slit and exposing the two components side by side on the same plate. Both lead to practically identical results and it is found that all the principal mercury lines of the visible region, *viz.*, λ4046, 4358, 4916, 5460 and the yellow doublet, in an initially unpolarised state, on transmission through the instrument acquire however a polarisation of 40%, the vertical component being weakened more than the horizontal. The result is probably correct to within ±5% and the variations with wave length do not seem to be so prominent as to produce changes greater than this figure. A computation based on Fresnel's equations, taking into consideration the situation of the prisms, in the instrument leads to a value very near the experimentally observed one. In order therefore to get the true polarisation of the Raman lines, the vertical component is always exposed for a longer time than the horizontal, the ratio of the exposures being 5:3. A plate containing graded exposures of the mercury spectrum is made use of in the evaluation of the ratio of intensities. The values given are relatively less accurate in cases of either very feeble or very intense lines.

3. *Results.*

The numbers in the brackets accompanying each frequency represent their relative intensities. ρ gives the ratio of the weaker to the stronger component, which may be termed the depolarisation of the particular frequency. The substances studied will be dealt with in different groups according to their structures.

Sulphur dioxide and carbon disulphide.—These two typical compounds are chosen to represent a triatomic molecule of the type AX_2. The differences between their Raman spectra, both in the number of frequencies and their characters are connected with the fact that CS_2 is a linear model whereas

SO_2	Frequency	526(0d)	1146 (10s)	1340 (0d)
	ρ	0·33	0·25	0·5
CS_2	Frequency	–	655 (10)	802 (2)
	ρ	–	0·25	0·25

SO_2 is a bent one.[5] It will be seen in the first instance that of the three frequencies in SO_2 the principal line which is marked by its extreme sharpness and great intensity is the best polarised, the degree of polarisation being the same as that of either of the CS_2 frequencies. Whether such a similarity in the polarisation characters implies any corresponding similarity in the nature of the three oscillations is at present very obscure. It must however be remarked here that corresponding to 1146 of SO_2 (8.73μ), a broad and intense infra-red absorption band has been recorded by Coblentz for this gas whereas CS_2 and CO_2 show no absorption in the infra-red corresponding to their principal Raman frequencies, *viz.*, 655 and 1284 respectively. This presumably implies that in the latter the oscillations involve no change in the electric moment, whereas in the SO_2 the great intensity of the absorption band suggests a considerable asymmetry of the oscillation. This may merely be the result of a difference in the geometry of the models and may not involve any essential difference in the characters of the oscillations. The other two weaker lines in SO_2 are less polarised and to different extents, suggesting that they represent distinct modes of oscillation.

Sulphur trioxide :—

Frequency :	290	370	534	666	697	1068	1271	1403	1489.
ρ	1	0·8	1	0·2	0·2	0·31	0·17	2	1

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[5] A case analogous to that of CS_2 is CO_2 in which frequencies 1264·5, 1285·1, 1387·7 and 1408·4 are observed in the gaseous state. See Dickinson, Dillon and Rasetti, Phys. Rev., Vol. 34, p. 582, (1929).

The case of sulphur trioxide affords an interesting example in that it contains at ordinary temperatures a certain proportion of polymerised molecules S_2O_6. Of the above frequencies 534, 1068 and 1403 are due to SO_3 and the others to S_2O_6. Here again the principal line at 1068 is well polarised whereas the one of frequency 534 is perfectly unpolarised. The third broad line at 1403 constitutes an anomaly in that the depolarisation is distinctly greater than unity. In fact in the polarisation picture of SO_3, reproduced in a previous paper by the author, this line is to be seen distinctly in the spectrogram taken with the vibration direction of the nicol horizontal whereas it is hardly visible in the one taken with the vibration direction vertical. A similar result has been noticed by Cabannes[6] in certain crystals, especially calcite, but this is the first instance of a liquid showing a Raman line with a depolarisation greater than unity. The Raman line corrésponding to this frequency and excited by the mercury line λ4046 shows however a different degree of polarisation, a result which is at the first sight very surprising. It so happens however that the antistokes component of an intense frequency 370 of S_2O_6 excited by λ4358 falls on this line and the apparent polarisation is evidently the resultant effect.

The Raman line corresponding to the largest frequency 1489 due to S_2O_6 shows an interesting structure in that it consists of a relatively bright and sharp central line with diffuse wings on either side. The central line is polarised to an appreciable extent whereas the accompanying wings are almost unpolarised. This no doubt suggests that the structure has a rotational origin but it is difficult to understand why it is prominent when associated with this frequency alone.

Ammonia :—

Frequency :	1070(od)	3216(2)	3304(4)	3380(1)
ρ	0·5	0·13	0·13	1

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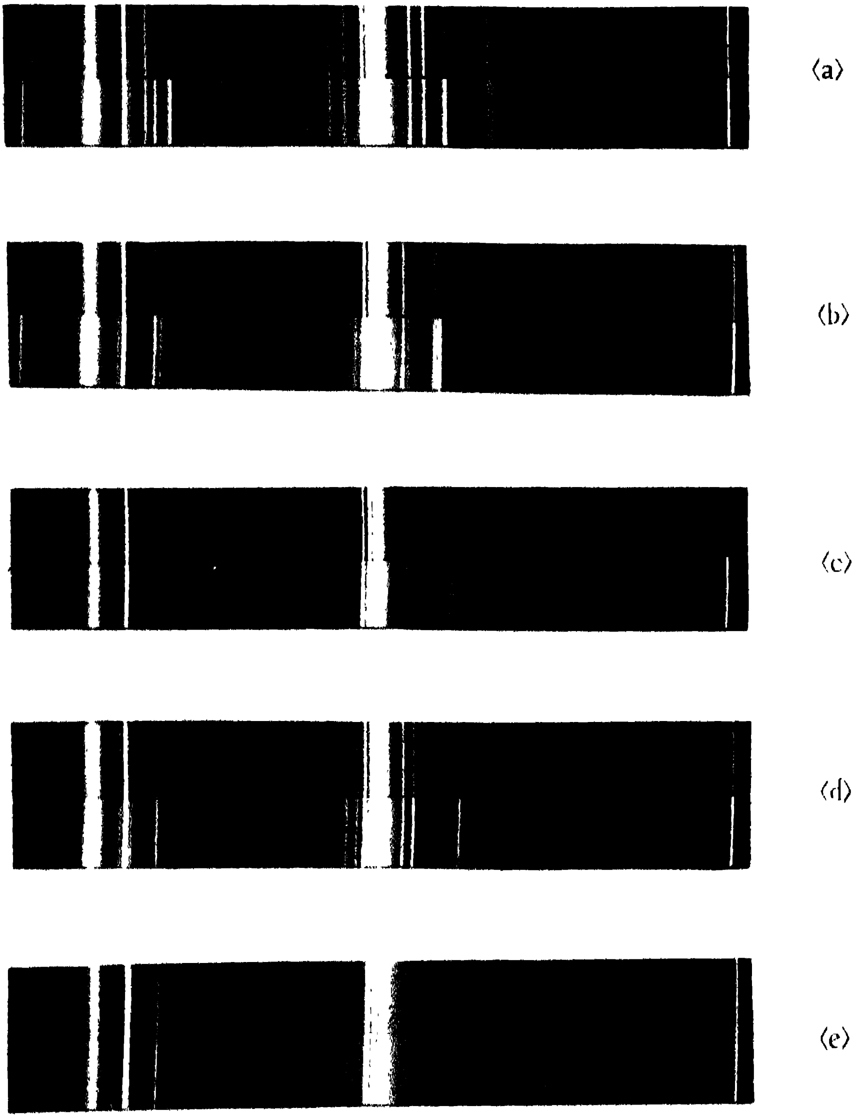
[6] Cabannes, *loc. cit.*

Polarisation of Raman Spectra.



(a) Carbon tetrachloride ; (b) Arsenic trichloride ,
(c) Phosphorus trichloride , (d) Bromoform , (e) Sulphur dioxide

In the polarisation picture of ammonia, reproduced in plate IV, it will be seen that of the group of four modified lines lying between λ4358 and 4916 lines of the mercury arc, the third is a broad and diffuse one presenting the appearance of a very imperfect polarisation. This is evidently due to the fact that two frequencies, *viz.*, 3216 excited by 4077 and 3380 excited by 4046 fall very near each other and give a superposed effect. The fact that 3380 is so imperfectly polarised contrary to the high degree of polarisation associated with 3216 is of great significance as it excludes the possibility of the components being due to a secondary Raman effect from the principal line 3304.[7]

Chloroform and bromoform :—

$CHCl_3$	Frequency :	263 (3)	366 (5)	668 (5)	768 (1d)	1222 (0)	1445 (0)	3025 (3)
	ρ	0·73	0·22	0·13	0.5	0·5	...	0·22
$CHBr_3$	Frequency :	154 (6)	222 (8)	538 (8)	654 (5b)	1146 (2)	1437 (0)	3023 (4)
	ρ	0·78	0·22	0·13	0·5	0·5	...	0·22

The line corresponding to a shift of about 1440 is so feeble in both cases that the polarisation could not be estimated with any certainty. The remarkable agreement between the spectra, their intensity relationships and their polarisation characters almost in every detail is too good a coincidence to be accidental, and is probably the strongest evidence in support of the view that they are all characteristic oscillations of the molecular model represented by CHX_3. The nature of X, its mass in particular, has very little influence on the general character of the radiations but as may be expected it loads the vibrating system resulting in a general diminution of the frequencies. It may be noted here that the third frequency given by 668 in chloroform and 538 in bromoform, is one of the most prominent ones and is the best polarised in both cases. The result is significant in that it suggests a resemblance to the AX_3 type, especially when the central atom is relatively lighter as in ammonia. This is intelligible if we regard the C-H group as replaced at its centre of gravity by a hypothetical atom of weight 13.

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[7] See J. B. Austin, Nature, Vol. 125, p. 464 (1930).

Trichlorides :-

PCl_3			$AsCl_3$			$BiCl_3$		
ν	I	ρ	ν	I	ρ	ν	I	ρ
190	10	0·88	159	8	0·86	96	8b	0·5
260	10	0·32	193	6	0·33			
488	2	0·75	370	6b	0·80	242	2b	0·75
512	10	0·14	410	10	0·17	288	10b	0·13

In the trichlorides of phosphorous and arsenic, it will be seen that the smallest frequency is very imperfectly polarised and the next in order comes the third which is however polarised to a small extent in both cases. The second one is fairly well polarised whereas the fourth is almost completely polarised (over 80%). In bismuth, the same general characters hold good except that the first broad band shows a value intermediate between those of the first and the second in the former cases, a result which obviously arises out of a superposed unresolved structure. The general similarity is again thus manifested very clearly in this series, the fluctuations from compound to compound in the actual values of the polarisation of any particular oscillation being surprisingly small especially if we remember that they constitute a very much larger range of variation in the masses of the vibrating parts than in $CHCl_3$ and $CHBr_3$ (P—31 to Bi—209).

Tetrachlorides:—

CCl_4			$SiCl_4$			$TiCl_4$			$SnCl_4$		
ν	I	ρ	ν	I	ρ	ν	I	ρ	ν	I	ρ
217	8	0·75	150	5	1	120	4	·8	106	5	1
313	8	0·8	221	5	0·9	145	0	0·83	131	6	1
450	10	0·1	426	10s	0·14	382	6	0·14	367	10	0·38
762	6	0·75	614	1d	1	494	0	0·5	403	6	0·8
792	6	0·75									
1537	2d	0·33	...	...	...	...	...	...	...	...	...

The polarisation characters of this series again show a strong resemblance between themselves as we pass from compound to compound. Ignoring the long shift of 1537 in CCl_4 we see that there are four frequencies in each case grouped into doublets, which are rather close in some cases. The general appearance of the spectrum thus resembles that of a trichloride. Contrary to this however, in these cases the third of the four Raman lines is the most prominent and the best polarised. The variation of both intensity and polarisation values for the different frequencies as we pass through the series is no doubt a little more marked here than in the case of either chloroform and bromoform or the trichlorides. The large discrepancy in the polarisation value given for 494 of $TiCl_4$ may partly be due to the extreme feebleness of the line. The case of CCl_4 however is slightly different from others in that the frequencies 217, 313 and the doublet at 770 show an appreciable amount of polarisation, whereas the corresponding frequencies in other cases are almost unpolarised. It is difficult to say if this is in any way connected with a probable anisotropic behaviour of the carbon atom itself.

The doublet at frequencies 762 and 792 is interpreted by the author as a single initially degenerate frequency which has split up into two components owing to a slight departure of the molecule from a tetrahedral symmetry. Such a common origin is supported by the fact that their polarisation characters are very similar. The significance of an extra line at 1537 is difficult to understand and its extreme feebleness no doubt suggests that it is a harmonic of the doublet at 770. The line, although diffuse, presents no doublet appearance and the different extent to which it is polarised is hard to reconcile with the view that it is a harmonic.

It may finally be remarked that the polarisation of the principal line shows a marked imperfection as we pass from carbon, the lightest, to tin the heaviest of the central atoms. Contrary to this however, Daure[8] finds the principal line in the tetrachloride of tin to be as completely polarised as in that of carbon. In view of this the author has obtained two independent photographs with this substance in both of which this line shows a considerable amount of depolarisation.

4. *Discussion of the Results.*

The following general characters may now be described. The polarisation of all the Raman lines shifted by any particular frequency from the different exciting lines is the same. When however two different frequencies excited by different mercury lines happen to overlap, then an average value is obtained.

The stokes and antistokes components are polarised to the same extent.

The depolarisation—ratio of the weaker to the stronger component—of the several Raman lines varies very widely ranging from 0 to 1.

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[8] Compt. Rend, Vol. 187, p. 940 (1928).

There is however one case, $\Delta\nu 1403$ in SO_3, whose depolarisation is greater than unity.

The general polarisation characters of the Raman spectra are very similar in compounds having analogous structures.

A high degree of polarisation is usually accompanied by a relatively large intensity although on the contrary it must be remembered that there are intense lines which are very imperfectly polarised.

The non-coherent nature of the Raman radiation[9] enables us to treat the problem of polarisation in a manner similar to the one adopted for the polarisation of Rayleigh scattering in gases, a state in which the mutual interference is so small that for all practical purposes the molecules act as independent sources of secondary radiation. The original explanation offered by Prof. Raman is based on the hypothesis that for a given energy transition, the molecule may be considered to have three principal directions with each of which is associated a different characteristic probability coefficient. Thus so far as the excitation of the molecule to a higher energy level is concerned it behaves as if it were an anistropic body, the degree of anistropy being different for different energy transitions. The coefficients of probability introduced here are in every respect analogous to the principal refractivities of the molecule in the theory of classical scattering and the above assumptions lead to an inherent depolarisation of every Raman line, the values ranging from 0 to $\frac{1}{2}$, the former representing the case, where the energy transition can take place with equal probability for all orientations of the molecule whereas the latter result is associated with a linear oscillator.

Of the subsequent attempts to give a satisfactory explanation of the phenomenon of polarisation, that of Cabannes may be mentioned here. From the theory of optical beats he has deduced a simple formula for a diatomic molecule involving the depolarisation of the classically scattered light. This leads to a depolarisation of about 10% and 4·5% for the Raman radiation in the cases of hydrogen and oxygen respectively. The range of variation is between 0 and $\frac{6}{7}$.

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[9] See papers by Bogros, Rocard and others on the subject.

Menzies attributed the two phenomena of complete polarisation and complete depolarisation to the cases where the direction of initial vibration is parallel and perpendicular respectively to that of the final vibration, intermediate inclinations giving rise to partial polarisation. This however presumes that two different vibrational energy levels are involved in the production of the Raman line. On the other hand in the quantum mechanical interpretation given by Hill and Kemble the polarisation of any Raman line is estimated by studying the relative magnitudes of the corresponding matrix elements associated with the three principal co-ordinate directions. A rough calculation made by them in the case of a diatomic molecule leads to a high degree of polarisation for Raman lines associated with vibrational transitions (about 80%). Besides the fact that the above theories lead us to such widely different conclusions a consideration of the actual experimental facts presents considerable difficulties in the way of a proper interpretation of this phenomenon. The tables will clearly show that there are values ranging from 0 to 1, and in one case the depolarisation is definitely greater than unity. The significance of the latter result is not at all clear.

Relation between intensity and polarisation.—As was remarked earlier, the well polarised lines are generally the intense ones—a result which will be more critically examined here. It is now known that for some reason, such oscillations as do not involve a change in the electric moment of the molecule come out with great intensity in the Raman spectra. The geometry of such oscillations, especially in the tetrahedral structures that are studied in this paper, is presumably represented by symmetric expansions and contractions of the tetrahedra; the probability of the corresponding energy transition being also symmetric in that it is independent of the direction to a large extent. The latter fact involves a large polarisation of such symmetric oscillations and is in agreement with the observations. The conditions that govern the intensity of the Raman lines are however not constituted by the symmetry or otherwise of the oscillations alone, as cases of intense Raman lines with correspondingly prominent infra-red absorption maxima are well-known. Consequently an intense Raman line may or may not involve a high degree of polarisation.

In connection with polarisation, it may finally be remarked that the great similarity, exhibited by members belonging to a series represented by any particular molecule model, which persists through a large range of atomic weights is a strong evidence in support of the view that the geometry of the oscillation is one of the principal factors that govern the state of polarisation of the scattered light. A simple picture of the relation is rendered difficult by the fact that the oscillations in most of the above cases are already very complex. A study of the various diatomic molecules of widely varying masses is evidently of great utility in affording a crucial test of several of the above observations and is now being undertaken by the author.

In conclusion the author desires to express his best thanks to Prof. Sir C. V. Raman for his kind interest and encouragement in the work. All the problems described in the paper have been taken up at his suggestion.

6

Raman Effect and Molecular Structure.

By

S. BHAGAVANTAM.

(*Received for publication, 5th May, 1930.*)

ABSTRACT.

On the view that a great majority of the Raman lines are caused by transitions corresponding to fundamental vibration frequencies of the molecules involved in the scattering process, an interpretation of the Raman spectra of various simple molecules is attempted on the basis of dynamical considerations. Following Dennison, suitable assumptions regarding the form of the energy functions have been made and the characteristic oscillations of models like X_2, X_3, X_4 and AX_2, AX_3 and AX_4 have been investigated. The theoretical results are correlated with those recently obtained by the author from a study of the Raman spectra in a number of simple molecules to which one or other of the above structures can be assigned.

All diatomic oscillators have one vibrational frequency, examples being those of H_2, N_2, O_2 and Cl_2. A system like X_3 arranged at the corners of an equilateral triangle, represented by ozone which however is not studied in this paper, has two fundamental frequencies. The model of X_4 has 4 and 3 frequencies respectively according as it is a square or a tetrahedron. The molecule of phosphorus is found to have three Raman frequencies and hence presumably a tetrahedral structure. The third of these is very prominent in the scattering and corresponds to a radial expansion of the tetrahedron.

AX_2 has 3 and 2 frequencies respectively according as it is a bent or a linear model. The cases of SO_2 representing the former and CS_2 and CO_2 the latter have been discussed. AX_3 has 4 frequencies and the equations are correlated with the typical cases of several trichlorides. The fourth frequency is usually a prominent one in the Raman spectra and is attributed to an oscillation of the central atom along the symmetry axis against the plane of the X atoms. When A happens to be very light, certain alterations are produced in the general features of the scattered spectrum, typical example being that of BCl_3 which shows only two Raman frequencies. The constants used in the evaluation of the frequencies indicate that the altitude of the pyramid increases progressively as we pass from phosphorus the lightest to bismuth the heaviest. AX_4 has again 4 frequencies and the equations are discussed with reference to the Raman spectra of various tetrachlorides. The third frequency which arises out of an isotropic vibration of the central atom within the tetrahedron comes out in the scattering with prominence.

From a general survey of all the models it seems clear that such of the oscillations as involve relatively small or no change in the electric moment of the molecule often manifest themselves very prominently in the Raman spectra.

1. *Introduction.*

The mechanism of the new phenomenon of light scattering has been pictured by Sir C. V. Raman immediately after the discovery in a simple manner wherein the incident quantum of radiation is supposed to exchange energy with the molecules with which it encounters and reappears as a scattered quantum of altered energy. If E_k and E_l represent two energy levels of a molecule, the frequency ν_{kl} given by $E_k - E_l/_h$ manifests itself in the scattered spectrum in the form of various Raman lines represented by $\nu_0 \pm \nu_{kl}$ where ν_0 is the frequency of the incident quantum of radiation. Apart from a small proportion of excited molecules, under the average conditons of experiment a great majority of them are in the normal or vibrationless state, and the transitions are therefore constituted mostly by changes of the form $0 \rightarrow 1$ in the vibrational quantum numbers. On this view most of the Raman transitions represent the fundamental vibration frequencies of the molecule involved in the scattering process. A correlation of the natural frequencies as revealed in the

Raman spectra with the molecular structure can therefore be effected through a study of the characteristic modes of oscillation of certain simple types of polyatomic models. From a purely dynamical point of view the subject has been first tackled by Dennison[1] who has investigated the systems of the type AX_2, AX_3 and AX_4 represented by special cases like CO_2, NH_3 and CH_4. The author has recently studied the Raman spectra of several simple molecules so chosen as may reasonably be represented by one or other of the molecular models X_2, X_3, X_4 or AX_2, AX_3 and AX_4. A brief consideration of each model will be given here. The general principles are the same as those originally adopted by Dennison.

2. *Theoretical considerations.*

A system of n particles will in general have $3n$ degrees of freedom and hence its configuration can be specified by $3n$ generalised co-ordinates, but if the system is subjected to the restriction that either rotation or translation as a whole is not permissible, then 6 of these $3n$ co-ordinates can be ignored, three associated with translation and three with rotation, and the rest, *viz.*, $(3n-6)$ can be chosen in a variety of ways. Under these conditions the potential and the kinetic energies of the system may be expressed as positive definite quadratic forms in the $3n-6$ co-ordinates and their time derivatives respectively.

It is known from the theory of vibrations that if the kinetic and the potential energies of a vibrating system are given in the form

$$T=\frac{m}{2}\,(a_{11}\dot{q}_1{}^2+a_{22}\dot{q}_2{}^2\ldots\ldots a_1 a_2\dot{q}_1\dot{q}_2\ldots\ldots);$$

$$V=\frac{1}{2}\,(b_{11}q_1{}^2+b_{22}q_2{}^2\ldots\ldots b_1 b_2 q_1 q_2\ldots\ldots)$$

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[1] Astrophys. Jour., Vol. 62, p. 84, 1925 and Phil. Mag., Vol. 1, p. 195 (1926).

it is always possible to find a linear transformation of the co-ordinates such that the energies, when expressed in terms of the new co-orinates, have the form

$$T=\frac{m}{2}\,(\dot{q}_1{}^2+q_2{}^2\ldots\ldots);\quad V=\tfrac{1}{2}\,(\mu_1 q_1{}^2+\mu_2 q_2{}^2\ldots\ldots)$$

μ_1, μ_2...being constants and the transformed co-ordinates q_1, q_2...being the normal or principal co-ordinates. The fundamental frequencies with which the system is capable of oscillating are given by $\frac{1}{2\pi}\sqrt{\mu_1}$...etc. The system may be treated as equivalent to a number of independent Planck oscillators whose characteristic frequencies are identical with the above normal modes of vibration. Following Dennison, the assumption that the fields of force are central about each nucleus will be made and we concern ourselves only with the oscillations about an equilibrium configuration, the displacements of the individual particles from their mean positions at any instant being infinitesimal; the assumed centro-symmetry of the electron configuration remaining practically undisturbed at the instant of each displacement. It will however have to be remembered that the actual state of affairs in a molecule is far more complicated and the above assumptions can only lead to an approximate theory.

3. *Polyatomic Molecules of Elements.*

X_2: It is clear that a diatomic oscillator has only one degree of vibrational freedom and hence has only one fundamental frequency of oscillation. Typical cases of hydrogen, nitrogen, oxygen and chlorine may be cited here as examples. The frequency shifts[2] as revealed in their Raman spectra, *viz.*, 4162, 2331, 1555 and 556[2] respectively are in almost perfect agreement with the primary oscillation frequencies in the normal states as calculated from band spectra data (4162,

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[2] The former three are due to Rasetti and the fourth, *viz.*, chlorine is taken from another paper by the author.

2331, 1554, 555). Such a result would suggest at once that the fundamental oscillation frequencies are involved in the production of a great many of the Raman lines. This view will now be further examined in more complex cases. In exceptional cases, however, a weak harmonic may be detected.

X_3 : For such a system 3 co-ordinates are necessary to represent the configuration at any moment and are chosen as the mutual displacements along the three sides of the triangle represented by q_1, q_2 and q_3. In accordance with the above assumptions, the energy functions may be written as

$$T=\frac{m}{2}\ \{P(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2)+R(\dot{q}_1\dot{q}_2+\dot{q}_2\dot{q}_3+\dot{q}_1\dot{q}_3)\}$$

$$V=\frac{k}{2}(q_1^2+q_2^2+q_3^2).$$

The coefficients can easily be evaluated by letting each co-ordinate vary independently and studying the consequent motion of the nuclei under the conditions that there is no resultant angular or linear momentum consistent with the ignoration of the 6 co-ordinates associated with translation and rotation of the system. The kinetic energy takes the form

$$T=\frac{m}{2}\left\{\frac{5}{9}\left(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2\right)-\frac{2}{9}\left(\dot{q}_1\dot{q}_2+\dot{q}_2\dot{q}_3+\dot{q}_1\dot{q}_3\right)\right\}.$$

The characteristic determinant whose roots determine the normal modes of vibration may be written as

$$\left(m\lambda-3k\right)^2\left(m\lambda-\frac{3k}{2}\right)=0 \qquad \ldots \quad (1)$$

and is of the third order and is evidently degenerate in that it has only two distinct roots. The normal frequencies of this system are therefore given by

$$\frac{1}{2\pi}\sqrt{\frac{3k}{2m}}\,;\ \frac{1}{2\pi}\sqrt{\frac{3k}{m}}$$

where k is a constant representing the binding force between any two atoms. The actual case in which the theory may be tested is that of ozone, the experimental difficulty in which case is considerable but the author however hopes to study it at a later date.

X_4 : The model of X_4 will next be considered. There are two probable arrangements of the nuclei in space namely, all the four being in the same plane and at the corners of a square, or in space at the corners of a tetrahedron. Six co-ordinates are necessary to specify the configuration and these will be chosen as the mutual displacements along the four sides and the two diagonals of the square in the former case and as the displacements along the edges themselves in the latter. The constants entering the kinetic energy functions can similarly be determined by allowing the co-ordinates to vary independently subject to the same restrictions as before and the functions written as

$$\mathrm{T}=\frac{m}{2}\left\{\left(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2+\dot{q}_4^2\right)+\frac{1}{2}\left(\dot{q}_5^2+\dot{q}_6^2\right)+\left(\dot{q}_1\dot{q}_2+\dot{q}_1\dot{q}_4\right.\right.$$
$$\left.+\dot{q}_3\dot{q}_2+\dot{q}_3\dot{q}_4+\dot{q}_1\dot{q}_3+\dot{q}_2\dot{q}_4\right)-\frac{5}{4\sqrt{2}}\left(\dot{q}_1\dot{q}_6+\dot{q}_4\dot{q}_6+\dot{q}_2\dot{q}_6\right.$$
$$\left.\left.+\dot{q}_3\dot{q}_6+\dot{q}_1\dot{q}_5+\dot{q}_2\dot{q}_5+\dot{q}_3\dot{q}_5+\dot{q}_4\dot{q}_5\right)\right\}$$

and
$$\mathrm{T}=\frac{m}{2}\left\{\frac{5}{8}\left(\dot{q}_1^2+\dot{q}_2^2+\dot{q}_3^2+\dot{q}_4^2+\dot{q}_5^2+\dot{q}_6^2\right)-\frac{1}{4}\left(\dot{q}_1\dot{q}_2\cdots\cdots\right.\right.$$
$$\left.\left.\dot{q}_5\dot{q}_6\right)+\frac{1}{4}\left(\dot{q}_1\dot{q}_6+\dot{q}_2\dot{q}_4+\dot{q}_3\dot{q}_5\right)\right\}$$

for the square and the tetrahedral models respectively. The characteristic determinant is of the sixth order in either case and may be written respectively as

$$\left(\lambda-\frac{2k_1}{m}\right)^3\left(\lambda-\frac{2k_2}{m}\right)\left\{5\left(\frac{m\lambda}{2}\right)+4\left(\frac{m\lambda}{2}\right)\left(k_1+5k_2\right)\right.$$
$$\left.-4k_1k_2\right\}=0 \qquad \ldots \quad (2)$$

and $$(m\lambda-2k)^3\,(m\lambda-4k)\,(m\lambda-k)^2=0 \qquad (3)$$

for the two models, k_1 and k_2 in equation (2) are constants representing the force between the atoms along a side and a diagonal of the square respectively. k in equation (3) represents the force between the atoms along the edge of the tetrahedron. The system is evidently degenerate in either case in that it has 6 degrees of freedom and has only 4 independent modes of oscillation for the square model and 3 for the tetrahedral one.

An actual case of such a system may be sought for in the molecule of phosphorus, P_4, whose Raman spectrum has been studied by the author. The entire spectrum arises out of three independent frequencies in accordance with a tetrahedral model, the actual values being 374, 468 and 607. Such an inference is in agreement with the fact that yellow phosphorus belongs to the cubic system of crystals. It will be seen from equation (3) that the frequencies are given by

$$\nu_1=\frac{1}{2\pi}\sqrt{\frac{k}{m}}\,;\quad \nu_2=\frac{1}{2\pi}\sqrt{\frac{2k}{m}}\,;\quad \nu_3=\frac{1}{2\pi}\sqrt{\frac{4k}{m}}$$

their ratio being $1:\sqrt{2}:2$. In the actual case however, the frequencies do not strictly conform to such a ratio, a fact which may be explained if we remember that the conclusions are subject to certain limitations especially if the distribution of the fields of force is more complicated than that assumed.

It will be interesting to note that the third of the three Raman frequencies observed is the most intense one which, as will be seen later, is the general result observed with analogous tetrahedral models of the kind AX_3 and AX_4. In both cases there are always four Raman lines, the third in the AX_4 and the fourth in the AX_3 being generally the most prominent. In fact from the linear transformations performed, it may be deduced that this frequency represents the oscillation in which the whole tetrahedron is expanding symmetrically, and it is significant that such an oscillation comes out with great intensity in the Raman spectrum.

We may now pass on to the more complicated systems with a central atom namely AX_2, AX_3 and AX_4. All the three cases have been worked out by Dennison and his equations will be adopted here. Several other investigators have tackled these systems by independent methods and arrived at practically the same conclusions.

4. *Triatomic Molecules.*

AX_2: The characteristic determinant for such a triatomic molecule may be written in the form

$$\left(\frac{m\lambda}{K_1}-1-\frac{2m}{M}\sin^2\alpha\right)\left\{\left(\frac{m\lambda}{K_1}\right)^2-2\left(\beta+\frac{1}{2}+\frac{m}{M}\cos^2\alpha\right)\frac{m\lambda}{K}\right.$$
$$\left.+\frac{2\beta\cos^2\alpha}{\mu}\right\}=0 \qquad \ldots \quad (4)$$

where

$$\beta=\frac{K}{K_1} \text{ and } \mu=\frac{M}{2m+M};$$

K_1 and K representing the binding between A and X and X and X respectively. M is the mass of A and m that of X. It will be seen that so long as α has a value other than 90° which is the case when the molecule is of a non-linear type, the system is non-degenerate and may be expected to give 3 independent vibrational frequencies. The equation was correlated by Dennison with the results obtained in the infra-red absorption of CO_2 on the assumption that it is a non-linear model, contrary to which however it is now well established that it is a linear molecule.[8] A molecule like SO_2, which is definitely known to be non-linear affords an interesting case. Its Raman spectrum is studied by the author from this point of view and the results are in excellent agreement with the theory in that it reveals three and only three independent oscillation frequencies corresponding to infra-red wave lengths 19·0, 8·73 and 7·46μ which presumably represent the fundamental frequencies of the molecule. It may be noted here that the gas has been found by Coblentz to exhibit two prominent absorption bands in the infra-red at 8·64 and 7·41μ in agreement with the above.[4] The region of 19μ is beyond the range of his investigation. There are three arbitrary constants entering into the characteristic determinant and hence the evaluation of the three frequencies will afford no unique proof of the theory. On the other hand the factors that govern the intensity relationships in the infra-red spectra are entirely different from those that are responsible for the Raman spectra and hence the arguments used by Dennison in the case of CO_2 for testing the theory cannot be employed here.

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[8] F. T. G. Rawlins, Mol. Structure and Mol. Spectra, Rep. of Faraday Society, p. 995 (1929)

The transformations performed in reducing the energy functions to their normal co-ordinates suggest, that of these three modes of oscillation, in the motion corresponding to the linear root of the characteristic determinant the sulphur atom vibrates in the plane of the triangle along a line perpendicular to the symmetry axis, the oxygen atoms remaining fixed, whereas in the motion corresponding to the other two roots, it vibrates along the line of symmetry, the oxygen atoms going apart or coming near each other symmetrically. An upper limit for the force between the sulphur and oxygen atoms may be deduced from a comparison of their dissociation energies in SO and SO_2. Making use of this limiting value for the constant K_1, a correlation of the observed frequencies with those contained in equation (4) is attempted and it is found that the linear root can be associated only with the lowest frequency namely 526, yielding a real value for α. The two larger frequencies 1146 and 1340 are obviously due to the sulphur atom vibrating along the symmetry axis, the more intense one corresponding to the more symmetric vibration.

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[4] J. Lecomte, Spectre Infrarouge, p. 320 (1928).

By putting $\alpha=90°$ in equation (4) it can be so modified as to be applicable to certain special cases where the three constituent atoms are all in the same line. The equation takes a form in which it has only two finite roots given by

$$\frac{m\lambda}{K'}=1+\frac{2m}{M} \text{ or } 2\beta+1.$$

Two typical molecules which are conspicuous for their non-polar nature are CO_2 and CS_2 and are particularly suitable for a study of light scattering from the above point of view. The very fact that both these molecules give only two principal Raman frequencies—the one analogous to the third at 526 in SO_2 being absent in both of them—may be connected with the linearity of the former unlike the triangular model of SO_2. Contrary to the case of SO_2, in neither of these substances has any absorption been recorded in the infra-red corresponding to the Raman frequencies. Various attempts have been made to interpret these frequencies, especially in CO_2, as due to difference combinations of the observed infra-red absorption bands. In the interpretation of the infra-red spectrum of CO_2 prominent ones at 2·72 4·25 and 14·47μ have been taken as fundamental oscillations, but such a view is now clearly untenable in view of the accepted collinear model for CO_2 which implies an inactive fundamental[5] and hence not manifested in the infra-red absorption. The case of CS_2 is entirely analogous and offers similar difficulties.

The appearance of two principal frequencies in these cases is no doubt in agreement with the above theory, but in both cases they are so close that a more detailed examination is necessary. In the first instance it may be stated that Rasetti has succeeded in observing two more feeble lines in the vicinity of the above in CO_2, and Krishnamurti has similarly recorded weak lines in CS_2 in the neighbourhood of the principal frequencies. Appearance of these new frequencies, although very weak, is in direct disagreement with the above theory. A study of the polarisation in CS_2 leads one to believe that all these Raman lines represent in reality only one oscillation, the principal or the unperturbed frequency being represented by the most intense line of the group, all the others being in essence slight modifications of the same. The modification may be introduced either by a readjustment, however slight it may be, of the electron configurations in the molecule itself or by a possible departure from perfect linearity in a small proportion of the molecules.[6] This assumes that the essential characters, geometrical or otherwise, of all these subsidiary oscillations to be largely akin to those of the principal one. This is not surprising if we remember a similar case of the frequency usually associated with the C—H bond which is often multiple in various complex compounds and it is hard to say if the phenomena are really analogous. In fact the entire infra-red spectrum of CO_2 for instance cannot be successfully explained on the view that these two are distinct and the only fundamental oscillations. It is also significant that such close companions have only been detected[7] in CS_2 and CO_2 whereas the analogous case of N_2O according to Rasetti, Dickinson and Dillon gives only one Raman line, a fact which may probably be connected with the presence of the carbon atom in the former molecules.

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[5] Eucken, Z. Phys., Vol. 37, p. 714 (1926). See also Ghosh and Mahanti, Phys. Zeit., Vol. 30, p. 531 (1929).

Such an explanation leaves us facing the problem of finding out the second frequency which is predicted by the theoretical model and yet undetected in either CO_2 or CS_2. The only explanation is that it is far too weak and diffuse to be detected under ordinary conditions, a view which finds support if we compare the relative intensities of the lines in the analogous case of SO_2 where the principal line **1146** is many times more sharp and intense than the other two diffuse and weak lines.

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[6] See McCrea, Proc. Camb. Phil. Soc., Vol 23, p. 890 (1927).

[7] Phys. Rev., Vol. 34, p. 582 (1929).

5. *The Trichlorides.*

AX_3: The atoms in this model are assumed to be at the apices of a pyramid. The characteristic determinant is given by Dennison in the form of the equation

$$\left\{ l^2-2\left(\frac{3}{2}L+\frac{1}{6}+\frac{c^2}{2\mu a^2}\right)l+\frac{3Lc^2}{\mu a^2}\right\}\left\{l^2-2\left(\frac{3}{4}L+\frac{1}{12}+\frac{b}{12\mu}\right)l+\frac{Lb}{4\mu}\right\}^2=0 \qquad (5)$$

where

$$l=\frac{m\left(c^2+\frac{a^2}{3}\right)\lambda}{k_1a^2}\ ;\ \mu=\frac{M}{3m+M}.$$

$$L=\frac{k}{k_1}\left(\frac{c^2+\frac{a^2}{3}}{a^2}\right) \text{ and } b=1+6\mu\frac{c^2}{a^2}$$

The system is again degenerate in that it has two double roots and hence only four independent modes of oscillation are possible although it has six degrees of freedom. c and a represent the height and the side of the basal triangle of the pyramid respectively. The other letters have the usual significance. Of these four frequencies, those corresponding to the linear roots, say ν_1 and ν_2, represent oscillations in which the central atom vibrates along the symmetry axis, while the X atoms move in or out symmetrically with respect to the axis of the pyramid. The double roots correspond to the oscillations in which the central atom vibrates normally to the symmetry axis.

Before discussing the validity of these conclusions the case of ammonia may be considered here in detail. It belongs to the type AX_3 under consideration and affords an interesting case in that its infra-red spectrum has been fully analysed by various investigators. The band at 10·5 μ is associated with the oscillation in which the hydrogen atoms recede from the symmetry axis as the nitrogen is approaching their common plane. This band is found to have a peculiar structure in that it has two close and prominent Q branches which is intimately connected with the fact that the altitude of the pyramid is very small and the nitrogen atom has two equilibrium positions, corresponding to two close minima in the potential energy function, one on either side of the plane.

On the other hand, the band at 3μ is associated with a similar vibration in which the three hydrogens and the nitrogen move in or out at the same time. Of the other two fundamental modes in which the nitrogen may be expected to move in directions normal to the symmetry axis, one may be identified with the band at 6μ in the infra-red absorption. It must be noted now that all these three fundamental oscillations are revealed in the Raman spectra at 3303, 1580 and 1070, the former coming out with relatively much greater intensity, a fact which is of great significance, as it will be seen that intense Raman lines in all the trichlorides represent just such oscillations in which the central atom moves against the plane of the X atoms as they keep going in or out symmetrically.

Going back to the equation (5), it will be seen that there are three constants entering into the equation which depend on the dimensions of the molecular model and also on the nature of the distribution of the interatomic forces; a correlation of the observed frequencies in such models with the theory can only be effected by assuming reasonable values for the same. The table below sets forth the calculated and observed values together with the assumed molecular constants which result in the best fit.*

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* When $BiCl_3$ is dissolved in strong HCl, the lines corresponding to the two lowest frequencies run together and form a band. The values given correspond to the edges of the unresolved band. Data for $SbCl_3$ are taken from Daure.

Substance		P^2	$k \times 10^{-4}$	$k_1 \times 10^{-4}$	ν_1	ν_2	ν_3	ν_4
PCl_3	Cal.	0·224	7	19	498	255	500	178
	Obs.				512	260	488	190
$AsCl_3$	Cal.	0·5	6	14	388	230	396	144
	Obs.				410	193	370	159
$SbCl_3$	Cal.	0·706	6	8·7	343	148	329	123
	Obs.				360	155	320	130
$BiCl_3$	Cal.	1·0	5	4·4	293	140	280	91
	Obs.				290	130	240	90

The table reveals many interesting features. The constant P which represents the ratio of the altitude of the pyramid to the side of the basal triangle increases as we go up the series P, As, Sb and Bi. Atoms like nitrogen, boron or aluminium which are lighter than phosphorus, the lightest in the series, may therefore be expected to form pyramids of low altitude approaching plane structures. The effect of such a relatively light central atom is manifested very clearly in the characteristic oscillations of certain molecules to be discussed a little later. The constant k_1 which represents the force between the central atom and the chlorine atom increases rapidly with decreasing atomic weight as may be expected. The variation is in qualitative agreement with the empirical rule suggested by Mecke from the band spectra data, *viz.*, $\nu\sqrt{z_1 z_2}=\text{constant}$, where ν is the frequency of oscillation of two bound atoms of atomic numbers z_1 and z_2. It must however be remembered that the rule is essentially intended for diatomic oscillators, whereas we are dealing here with oscillations of a much greater complexity.

Unlike this, the constant k which represents the force between the chlorine atoms themselves shows from compound

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Z phys., Vol. 42, p. 890 (1927).

to compound very little variation. This result may be interpreted as suggesting that their mutual distances remain practically unchanged, the variation in P being largely due to a variation in the altitude of the pyramid itself.

Mention may now be made of a special case of the AX_3 type wherein the A atom happens to be in the plane of the X atoms. As examples the cases of carbonates and nitrates may be cited. Several investigators have computed the frequencies of such a system on theoretical basis.[9] Special mention may be made of Nielsen who has followed up the methods originally adopted by Dennison. The four fundamental oscillation frequencies demanded by the theory for such a system come out in the Raman spectra of all nitrates and carbonates. Particular mention may here be made of the oscillation in which the three X atoms contract and expand symmetrically, hence producing no change in the electric moment of the molecule. Such an oscillation causes no direct absorption in the infra-red but it is just this that comes out with great intensity in the Raman spectra.

6. *Some Special Cases.*

NH_3, $CH\,Cl_3$, $CH\,Br_3$, $Al\,Cl_3$, $N\,Cl_3$, and $B\,Cl_3$[10] :—Special cases of AX_3 where A is relatively lighter are found in the above molecules. Such an exceptional character of the central atom is bound to produce alterations in the general characters of the Raman spectrum. It will first be noticed that whereas the fourth of the four frequencies always comes out with prominence in the Raman spectra of the trichlorides of P, As, Sb and Bi, NH_3 however gives only three, the third being the most intense. The fourth one is presumably very weak and hence not detected. As mentioned before the analysis of the motion in each case reveals that the intense Raman line in all the cases including ammonia arises out of an essentially the same oscillation; the one in which the central atom vibrates along the symmetry axis, the X's preserving symmetry about it.

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[9] Amongst others see H. Kornfeld, Z. phys., Vol. 26, p. 205 (1924) and H. H. Nielsen, Phys. Rev., Vol. 32, p. 773 (1928).

[10] $CHCl_3$ and $CHBr_3$ can be classed under AX_3 if the (CH) group is treated as one unit.

Such an anomalous reversal of intensities in ammonia is presumably connected with the low atomic weight of the nitrogen atom. In addition to such a reversal, it will be noticed from the table that with the decreasing weight of the central atom in the trichlorides, the forces between the chlorines and the central atom are becoming relatively more prominent than those existing between the chlorines themselves, a state of affairs which in the limiting case would result in the disappearance of two of the frequencies as may be seen by putting $k=0$ in the equation (5). Such a case is actually met with in that of boron, the lightest of the trivalent elements. This trichloride reveals only two frequencies 255 and 471[11] the second one being more prominent, evidently corresponding to the intense Raman line (the fourth if the central atom is heavy enough or the third if it is light) in this series of compounds. Data are however not available for the cases of aluminium and nitrogen. Chloroform and bromoform show similar results in that besides the frequencies which may be attributed to hydrogen, they give a spectrum consisting of four principal frequencies which fall into two rather close groups, the third one being relatively more prominent than others. There is however a fifth frequency in both these cases whose presence is difficult to understand on the above theory, a case which is in many respects analogous to that of an additional frequency in CCl_4 at about 1500. If this result is in any way connected with the common anisotropic carbon atom is more than what can be said from the available evidence.

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[11] Unpublished results of the work done by the author in collaboration with Mr. S. Venkateswaran.

Another interesting fact may here be noted, *viz.*, the violently explosive character of NCl_3 unlike the trichlorides of P, As, Sb and Bi. Data regarding the heats of formation of the various trichlorides are in agreement with the above anomalous behaviour of nitrogen chloride, in that its formation from nitrogen and chlorine is an endothermic reaction unlike that of all the other trichlorides which is exothermic. This is not surprising if we remember that the first member of a series in the periodic table often differs from its companions. Such an endothermic formation of the molecule and the explosive character must in some way be connected with the molecular model, which presumably differs from the usual tetrahedron.

7. *The Tetrachlorides.*

AX_4 : The system possesses nine degrees of freedom and is degenerate by virtue of its high degree of symmetry in that it has four normal frequencies given by—

$$\frac{1}{2\pi}\sqrt{\frac{k_2}{m}}\left(4\alpha+1\right)^{\frac{1}{2}}\ ;\quad \frac{1}{2\pi}\sqrt{\frac{k_2}{m}}\left(\alpha-\frac{\beta}{4}\right)^{\frac{1}{2}}$$

$$\frac{1}{2\pi}\sqrt{\frac{k_2}{m}}\left[\alpha+\frac{5}{9}-\frac{13}{36}\beta+\sqrt{\left(\alpha+\frac{5}{9}-\frac{13}{16}\beta\right)^2-\left(\frac{8}{9}\alpha-\frac{16}{9}\alpha\beta-\frac{10}{9}\beta-\frac{4}{9}\beta^2\right)}\right]^{\frac{1}{2}}$$

$$\frac{1}{2\pi}\sqrt{\frac{k_2}{m}}\left[\alpha+\frac{5}{9}-\frac{13}{36}\beta-\sqrt{\left(\alpha+\frac{5}{9}-\frac{13}{16}\beta\right)^2-\left(\frac{8}{9}\alpha-\frac{16}{9}\alpha\beta-\frac{10}{9}\beta-\frac{4}{9}\beta^2\right)}\right]^{\frac{1}{2}}$$

where $\alpha=\frac{k_1}{k_2}$ and $\beta=\frac{k'}{k_2}$; k_1, k_2 and k' are constants.

These are arbitrary and enter in the potential energy function. In the motion associated with ν_1 the tetrahedron expands or contracts symmetrically, the central atom remaining fixed at the centre of gravity; in that coresponding to the double root ν_2 the X atoms move on the surface of a sphere. The Planck oscillators connected with ν_3 and ν_4 may be treated as isotropic in that they are triple roots of the determinant. This isotropic character is no doubt the result of a high degree of symmetry imposed on the theoretical model, a departure from which may be expected in the actual molecules resulting in a splitting up of any one or all of the three degenerate frequencies ν_2, ν_3 and ν_4. Here again three constants enter the equations and hence an evaluation of the frequencies which are four in number may be achieved only by assuming suitable values for the same.

As typical instances, a detailed investigation of the light scattering in the tetrachlorides of carbon, silicon, titanium and tin is conducted and the results will be discussed here in the light of the above theory. It will be seen from the table given by the author in another paper that all these substances (with the exception of CCl_4) give four and only four Raman frequencies in entire agreement with the above theory which in itself is sufficiently convincing proof that these represent the fundamental oscillation frequencies in these molecules. Besides, the general characters such as the intensity and the polarisation relationships follow the same order in all these compounds. It will first be seen that the four Raman lines fall into two groups giving the spectrum an appearance of two rather close doublets in every case. Such a distribution of frequencies follows naturally from the model. To illustrate this, the case of CCl_4 will be considered in detail. The constant β is directly connected with the nature of the forces between the X atoms and it assumes a limiting value of zero if besides the Coulomb forces there are also electronic configurations perfectly symmetrical about each of the X atoms. It is interesting to note that the best fit with the observed values could be achieved only when β is made to take the limiting value zero. The constants k_1 and k_2 representing the forces between the carbon and the chlorine atoms themselves respectively are given the values 16×10^4 and 15×10^4. The calculated frequencies are given in the table below together with the observed ones.

CCl_4

Frequency	ν_1	ν_2	ν_3	ν_4
Calculated	290	770	154	459
Observed	310	770	216	459

As we proceed up the series, the same phenomenon as in the case of the trichlorides namely, a continual diminution of all the characteristic frequencies takes place which may be expected if they are really the fundamental oscillations in view of the fact that the vibrating system is being loaded with central atoms of increasing atomic weight. The doublet distribution of the frequencies is however preserved in every case. Of the above four frequencies ν_1 and ν_2 represent oscillations in which the chlorine atoms alone are taking part, the latter being a double root in the theoretical model. It will be seen that in the actual case of CCl_4 it has split up into two different frequencies of more or less equal intensity, a case of great significance which may be taken as an evidence for a slight departure of the molecular model from a perfect tetrahedron. The other tetrachlorides however show nothing of the kind and offer a unique support to the above theory in that the entire Raman spectrum in each case can be interpreted as arising from four and only four fundamental frequencies, combinations between themselves or overtones being absent in all cases. In the oscillations corresponding to ν_3 and ν_4 the carbon atom vibrates about its mean position, the probability of excitation being the same in all directions as each arises out of a triple root of the determinant. Special mention need be made here of one of these namely ν_4, which is particularly intense in all the four cases.

As further examples of this model, several cases may be suggested. Some of them namely, SO_4, ClO_4, MnO_4 etc., in the ionic state will be briefly considered here. The structure of these ions is presumably tetrahedral with the oxygens situated at the corners of the tetrahedron. It is interesting to note that the Raman spectra of aqueous sulphates and perchlorates are very similar to each other and are in perfect agreement with the above considerations. In table below, data taken from Taylor are given [12]

SO_4	450	614	989	1218
ClO_4	453	614	937	1140

The dynamics of such a system is quite the same as for AX_4 model and by analogy it may be concluded that the third frequency, which is also prominent in the above cases, is due to the central atom vibrating about its mean position within the tetrahedron. The case of MnO_4 is exceedingly interesting as a prominent vibration frequency of 785 is observed by Taylor [13] and by independent arguments he concludes that this represents an oscillation of the manganese atom within the tetrahedron.

8. *Variation of the principal frequencies with environment.*

As may be expected the free oscillations of the above groups are only present in the ionic state and differ from those of the unionised molecules to an extent depending on the restrictions which the hydrogen in the acids or the metal atom in the salts is capable of imposing on the freedom of the group. Even the oscillations of the free ion are appreciably influenced by the distribution of the surrounding molecules in a solvent, the influence varying considerably with the nature of the solvent. [14] This alteration which is of a relatively small magnitude does not affect the foregoing discussion, as every ion (SO_4, ClO_4, CO_3, etc.) in combination continues to manifest its characteristic frequencies which still (except for the above noted small difference due to the combined atom) follow the same general relationship of intensity and magnitude.

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[12] Rep., Faraday Society on Mol. Spectra and Mol. Structure, p. 830 (1929).

[13] *Ibid.*........p. 860 (1929).

[14] See Taylor, loc. cit.

A different kind of influence is seen in the interesting series of SO, SO_2, SO_3 and SO_4. As we go up the series, the obvious inference is that the increasing oxygen atoms result in an increasing complexity accompanied by a greater number of degrees of freedom. The table below illustrates the interesting points.

SO			1117*	
SO_2		526	1146	1340
SO_3		534	1068	1403
SO_4	450	614	989	1218

The frequencies given in the table, except for SO, are all obtained from a study of the Raman effect. Nisi[15] has however recently reported two additional lines in 10% H_2SO_4 corresponding to 893 and 1046 of which the latter is somewhat prominent. Such a result may be due to the fact that either the tetrahedron of the SO_4 ion has an intrinsic imperfection or is influenced very easily by the surroundings. This view is in accordance with the fact that there are striking variations in the frequencies of the ion with increasing dilution. The approximate agreement between the principal frequency 1146 of SO_2 and 1117 of SO is of significance if we remember that the calculated energy of dissociation of sulphur and oxygen from the band spectra data of SO is 148 kilo calories whereas the energy of dissociation as determined from the decomposition of SO_2 is 146·3 kilo calories.[16] Contrary to this however, as we pass on to SO_3 and SO_4 there is a definite diminution of this principal frequency.

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* The frequency is taken from band spectra data. See V. Henri and F. Wolff, Jour. De. Phys., Vol. X, p. 81 (1927).

[15] Jap. Jour. Phys., Vol. 5, p. 119 (1929).

9. *Relation between intensity and the character of oscillations.*

A comprehensive survey of the intense Raman lines in all the models discussed before in relation to the characters of the corresponding oscillations reveals interesting results. The principal lines in the cases of AX_2 and AX_3 are caused by the oscillations of A along the symmetry axes, the X's in either case preserving symmetry about them. The oscillation is therefore one in which there is a more or less symmetric expansion or contraction of the molecule as a whole. Similarly the intense line in the tetrahedral model of X_4 is attributed to a symmetric motion of the nuclei along the radial lines. All these cases involve relatively small or no change in the electric moment of the molecule as a whole and hence cause only weak absorption in the infra-red. Such of these oscillations are termed optically inactive and can only be detected indirectly when they combine with an active oscillation giving rise to absorption. Typical cases of such oscillations are presented by the principal Raman lines in the nitrates and carbonates. The result is not in any way surprising if we remember that the conditions which determine the intensity of a Raman transition are quite different from and much more complicated than those that are responsible for infra-red absorption. In fact, according to the wave-mechanical interpretation given by Hill and Kemble, a Raman transition corresponding to $E_k - E_l$ can always take place if there is a third energy level existing *simultaneously* with E_k

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[16] V. Henri and F. Wolff, *loc. cit.*

and E_l with which both of them can combine even if the direct transition $E_k \longrightarrow E_l$ is forbidden by the usual selection rules. The intensity depends on the nature and the number of the third levels with which the initial and final ones in the Raman transition can combine. It is however not clear why the case of a symmetric oscillation is particularly favourable for the appearance of a prominent Raman line.

Unlike these cases, the principal line in the tetrachlorides and other molecules of the type AX_4 is attributed to a three-dimensional oscillation of the central atom within the tetrahedron. This oscillation involves an appreciable change in the electric moment of the molecule and causes direct absorption in the infra-red. In estimating the intensity of absorption for such frequencies, Dennison takes the *a priori* probability of such states to be 3 times that of a state represented by single roots of the characteristic determinant. Such oscillations may be expected to come out quite as prominently in the infra-red absorption unlike the previous cases of symmetric ones. As examples the cases of SO_4 and ClO_4 may be cited.[17] So far as the Raman spectra are concerned the oscillation can be interpreted as one which can be excited along all the three co-ordinate directions with equal probability, such a transition giving rise to a prominent and well-polarised Raman line.

In conclusion the author desires to express his best thanks to Prof. Sir C. V. Raman for his kind interest in the work.

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[17] See Taylor, *loc. cit.*

7

The Raman Effect in Diamond

BY

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Madras University Research Scholar in Physics.

(*Received for publication, 12th May, 1930.*)

(Plate VI)

1. *Introduction.*

A study of the Raman effect in crystals has afforded interesting examples for inter-comparison of data relating to frequencies of the molecule calculated from the Raman spectrum, with those obtained by direct infra-red measurements. The case of quartz is typical. The Raman line corresponding to 8·5μ[1] which is very strong in the infra-red (reflection from a crystal), is so feeble that it is barely detectable even in the most well-exposed plates. Again, observations on cubic crystals [2] like NaCl, NaF, LiF, etc., whose rest-strahlen frequencies have been previously well-studied do not seem to exhibit any Raman lines.

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[1] K. S. Krishnan, Ind. Jour. Phys, Vol. IV, p. 138, 1929.

[2] C. Shaefer, Zeit. fur. Physik. 54, 153, 1929.

It was with a view to understand this aspect of the subject in greater detail, that the study of the Raman effect in diamond was undertaken.[1]

2. *Experimental methods and results.*

The method adopted to photograph the Raman spectrum was quite the same as that employed by other workers for crystalline solids. The diamond, which was quite a small one ($\frac{1}{2}$ carat size)—perhaps the smallest volume that has been so far used to photograph a Raman spectrum—was fixed to a thick copper plate, previously completely blackened on its surface. Light from a Hewittic quartz mercury lamp was focussed on to the diamond by means of a large condenser, and the transverse scattered light from the latter, focussed on to the slit of a Hilger constant deviation spectrograph. An E_2 quartz spectrograph was also used whenever it was available. By means of suitable diaphragms, direct light from the mercury arc as well as the reflected light from the facets of the diamond were avoided. With the complete mercury spectrum incident, using Ilford Iso-Zenith plates 700 H.D., an exposure from 10 to 15 hours was found sufficient to give a satisfactory spectrogram.

Fig. 1 in Plate VI reproduces the photograph obtained in the way indicated above. The plates were measured on a Hilger travelling microscope, and the wave-lengths of lines calculated with the known mercury lines on the plate as standards, and using the simplified form of Hartmann's interpolation formula.

The analysis of a typical plate is given below.

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[1] Ramaswamy, Nature (under publication as a preliminary note).

TABLE I,

Diamond.

Exciting Mercury Lines			Raman Lines			
Wavelength A.U.	Wave-number (in vacuo) per cm.	Intensity	Wave-length A.U.	Wave-number (in vacuo) per cm.	Intensity.	Difference in wave-numbers
3650·1	27389	100	3836·3	26059	0	1330
4046·6	24705	100	4277·3	23372	2	1333
4358·3	22938	200	4627·0	21606	4	1332

A diffuse band at 4156·8 A.U. very weak in intensity — Identified as a fluorescent band

3. *Fluorescence of diamond.*

For purposes of identifying the nature of the *diffuse band* in the Raman spectrum, it was found convenient to allow certain radiations alone to be incident on the diamond. With the filters placed between the condenser and the diamond, much longer exposures were found to be necessary.

The following filters were found to be suitable, and were therefore used.

(1) A strong solution of quinine sulphate (acidified slightly with H_2SO_4) followed by a blue glass. This served to suppress all the lines in the incident spectrum, except the 4358·3 A and its close companions. The solution had to be renewed every ten or twelve hours, since it gradually turned yellow due to the action of the light.

(2) A strong solution of cobalt sulpho-cyanate. This served to suppress all the lines in the ultra-violet, and the visible region except the group at 4046·6 A.U.

[1] The wave-length of this diffuse band was given approximately as 4155A. U. in the communication to Nature.

The diffuse band was identified as a flourescent band, as it was found that it appeared on the plate, both when the complete spectrum was incident and when the 4046·6 A group of lines were incident, but *not* when the 4358·3 A group alone was incident, (Fig. 2 and 3 in Plate VI). These observations were further confirmed by a study of the polarisation of the new lines, which will be described later.

4. *The rest-strahlen frequency of diamond.*

We can compare the value of the rest-strahlen frequency as calculated from the Raman spectrum with that deduced from the specific heat data, (as there seems to be no direct experimental observations on the same).

The best deduction of the characteristic frequency is that by E. Schrodinger[1] who discussed all the available data regarding the substance. He finds out that value for the characteristic frequency which would get the best fit with the specific heats over a large range of temperature (30°-1169°) on the most reliable theory (Debye's) that could be applied in this particular case. The method of calculating the characteristic frequency depends therefore on the specific heat measurements themselves. The formula he used to obtain the frequency is that of Gruneisen[2]

$$\nu_0 = 2{\cdot}91 \times 10^{11} \sqrt{\frac{1}{aV_0^{\frac{3}{2}}} \left(\frac{C_v}{\frac{1}{v} \cdot \frac{dv}{dT}} \right)}.$$

a=atomic weight

$V = a/\rho$

He finds for $\frac{h\nu}{k}$ the value 1860 corresponding to a frequency $38{\cdot}9 \times 10^{12}$. This can be compared with $40{\cdot}0 \times 10^{12}$ which we have obtained from the wave-number shifts of the Raman

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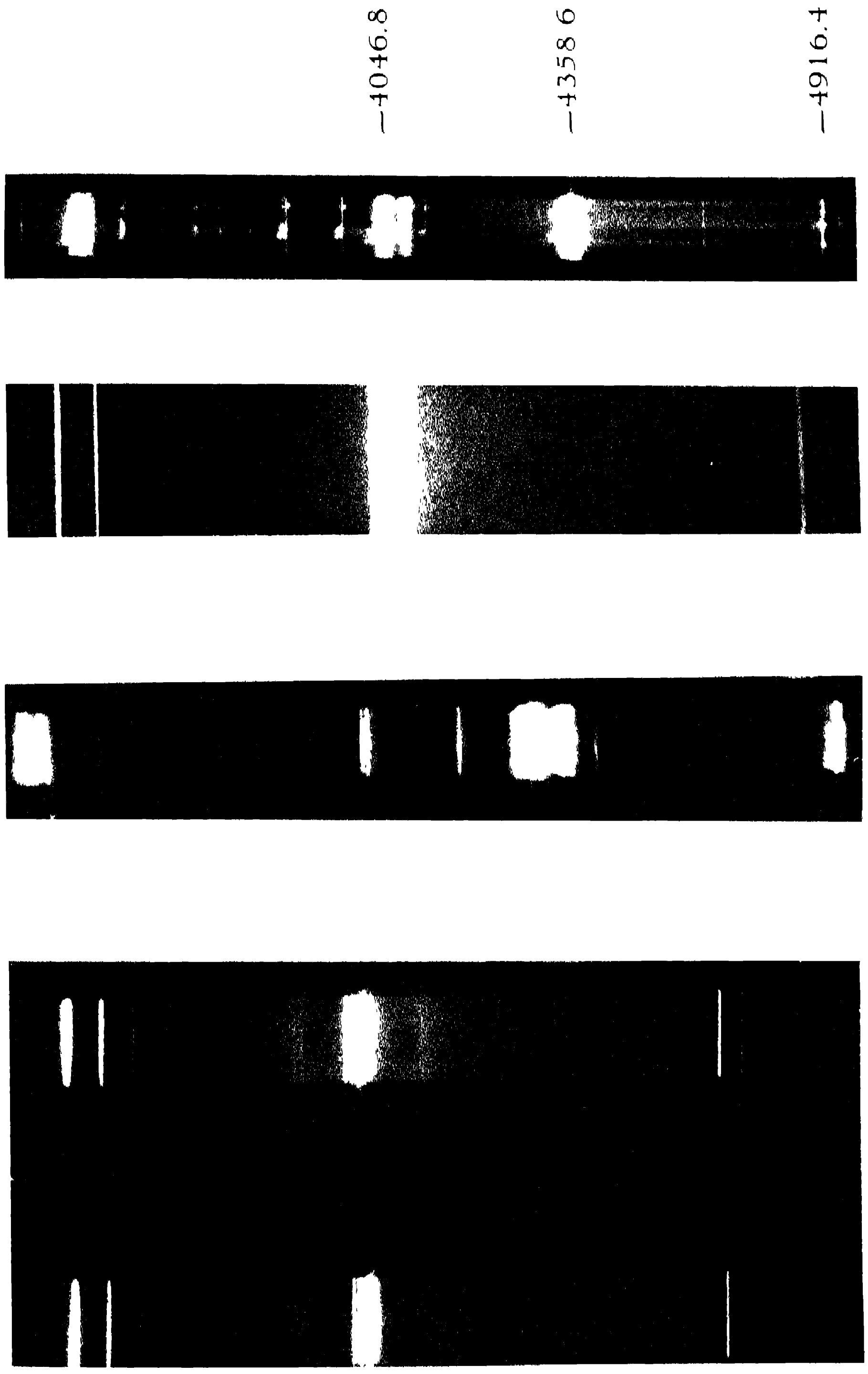
[1] E. Schrodinger, Physik. Zeits. 420, 450, 474, Vol. 20, 1919.

[2] Gruneisen, Ann. der. Physik. (4) 39,257, 1912.



Raman Spectra of Diamond.

lines. The difference of about 2·7 per cent. is not beyond the experimental inaccuracies of the specific heat measurements, particularly at low temperatures; *e.g.*, the rest-strahlen frequency of CaF_2 by direct measurement is $53·1 \times 10^{-4}$ cms., but that which is deduced from specific heat data is $51·0 \times 10^{-4}$ cms. This agreement has been considered satisfactory.

It is of interest to note here that the rest-strahlen frequency calculated from the empirical formula of W. Nernst and Lindemann[1]

$$C_v = \frac{3AR}{2}\left[\frac{x^2 e^x}{(e^x-1)^2} + \frac{\frac{x^2}{4} \cdot e^{\frac{x}{2}}}{(e^{x/2}-1)^2}\right]; \qquad x = \frac{h\nu}{kT}$$

comes out to be $40·0 \times 10^{12}$ which is *precisely* the value we have obtained. The perfect agreement must be to a large extent *accidental.*

5. *Polarisation of the scattered radiations.*

The polarisation of the lines in the scattered spectrum was also studied. For this purpose, two spectrograms were taken with equal exposures and under identical conditions, side by side on the same plate, using a large Nicol in front of the slit of the spectrograph. During one exposure the shorter diagonal of the Nicol was parallel and in the other perpendicular to the axis of incidence of the light on the diamond.

Fig. 4 in Plate reproduces a typical photograph obtained. A study of the photograph leads to the following conclusions :

(1) The unmodified lines are all partially polarised.
(2) The Raman lines are strongly polarised.
(3) The diffuse band (fluorescent) is unpolarised.

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[1] W. Nernst and N. Lindemann, Zeits. fur. Phys. Chem. P. 822, Vol. 17, 1911. Schrodinger (*loc. cit.*).

Also J. W. Mellor, Inorganic and Theoretical Chemistry, Vol. 5, p. 770.

This further confirms our previous identification ; it is well known that whereas the Raman radiations are strongly polarised, fluorescent radiations are generally unpolarised.

6. *Effect of temperature on the Raman radiations.*

In the original photographs the anti-Stokes lines corresponding to the excitation by 4358. 3A, 4046. 6A, and 3650.1 A could not be detected. This is naturally to be expected in view of the large wave-number shifts of the Raman lines, and the exponential relation between the intensities of the stokes and the anti-stokes lines. As the temperature of the substance is raised, one should naturally expect the anti-stokes lines to brighten up, since the proportion of molecules in a higher energy level increases with the temperature.

For the purpose of studying the effect of temperature, the following arrangement was decided upon, after a number of trials.

The copper bar carrying the diamond was mounted immediately above an ordinary electric heater. The temperature of the diamond was noted by an ordinary mercury thermometer and was found to be stationary at 250° C. Since the anti-stokes line corresponding to the excitation by 4358·3A would fall in the close proximity of the fluorescent band, the lines in the ultra-violet as well as the group at 4046.6A were suppressed by a quinine sulphate filter and the 4358.3 group alone was allowed to be incident on the diamond. Plates taken under identical conditions (1) with the diamond at laboratory temperature and (2) at 250° C indicate the following results.

(1) The Raman lines are not *perceptibly* shifted or decreased in intensity or degree of sharpness.

(2) No unambigous evidence of the presence of the anti-Stokes line could be obtained on the plate—indicating the insufficiency of rise of temperature to bring out the line to an order of perceptible intensity.

7. *Relation to crystal structure.*

It remains now to discuss the Raman effect in this crystal in relation to its crystal structure. Diamond is a *very perfect* crystal. The *great sharpness* of the Raman lines obtained in our experiments, is very well understandable in view of its great perfection.[1] The remarkable intensity of the lines is also to be expected in view of the ease with which organic substances seem to exhibit the Raman effect.

It has been shown by methods of X-Ray analysis[2] that the crystal structure of diamond corresponds with a lattice with carbon atoms arranged in two inter-penetrating face-centred cubic lattices, so that each carbon atom of the one is surrounded by four carbon atom of the other, with tetrahedral symmetry. Let us as comparison take the case of rock-salt. In this crystal the sodium and chlorine atoms are arranged in two intersecting face-centered cubic lattices, such that each sodium atom is centro-symmetrically surrounded by six chlorine atoms, and *vice versa*.

It has been suggested by C. Schaefer[3] that the non-appearance as Raman lines of the rest-strahlen frequencies of NaCl, KCl, etc., might be due to the *symmetrical* nature of the possible oscillations in the crystal lattice. The crystal structure of diamond differs from that of rock-salt in as much as we do not in the former have the same type of symmetry as in the latter. That the rest-strahlen frequency comes out with great intensity in diamond may well be related to this fact.

Diamond is a striking example of a crystal in which the nature of the binding forces between the atoms in the lattice are essentially of a homopolar type. In sodium chloride and its isomorphs the binding forces are of an electro-static type ; the sodium and chlorine atoms being completely separated ions are held together by electro-static forces. In diamond, on the other hand, the carbon atom has a tendency to combine with the carbon atoms surrounding it to form stable electron systems by holding electrons in common.

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[1] Sir C. V. Raman, Molecular Spectra and Molecular Structure, Farad. Soc. Report, 1929.

[2] X-Rays and Crystal Structure, by W. H. Bragg and W. L. Bragg. G. Bell & Sons, p. 99.

[3] C. Schaefer, Zeit. fur. Physik. 54, 153, 1929.

Whether the appearance of the rest-strahlen frequency of diamond as Raman lines, and their non-appearance in the case of NaCl, etc., is to be attributable to the dissimilarity in their crystal structure or in the essential difference in the nature of their binding forces, is more than one can say at present and can be settled only by further research.

8. *Summary and conclusion.*

The Raman spectrum of diamond was photographed. Intense and sharp Raman lines corresponding to wave-number shifts of 1332^{-1} cms. were obtained. This is in satisfactory agreement with the characteristic frequency deduced by E. Schrodinger from the specific heat data. Apart from the Raman lines a diffuse band was also detected at 4156.8 A. This was identified to be of fluorescent origin by irradiating it by monochromatic radiations, one on the longer and one on the shorter wave-length side of 4156.8A. The polarisation of the Raman lines was tested and the latter found to be strongly polarised. The effect of temperature was also studied, and the results are discussed in relation to crystal structure.

In conclusion, I wish to express my heart-felt thanks to Sir C. V. Raman, F. R. S., at whose suggestion this work was undertaken. I also wish to express my most sincere thanks to Dr. H. P. Parameswaran for the constant encouragement and the continued interest he has been taking during the entire course of this work. My sincere thanks are also due to Prof. V. Appa Rao of our department, for the very great interest he has been taking in my work.

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10th May, 1930.

8

Raman Spectrum and Infra-red Absorption of Sulphur

BY

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(Plate VII)

(*Received for publication, 21st June, 1930*)

ABSTRACT.

The Raman spectrum of rhombic sulphur in the form of small crystals has been examined with the 5461A mercury line isolated by a didymium filter. Four prominent lines and two faint ones were observed ($\nu_0=85$ cm^{-1}, $\nu_1=152$, $\nu_2=216$ $\nu_3=470$, $\nu_4=243$ and $\nu_5=434$ respectively). In a solution in carbon di-sulphide only ν_1, ν_2 and ν_3 were found, ν_1 and ν_3 being slightly different ($\nu_1=149$ cm^{-1}, $\nu_3=474$) from those of the crystal. ν_0 is attributed to the S_{16} molecule in the crystal, and its absence in solution shows the presence of smaller groups (S_8). It is shown that the infra-red measurements of Taylor and Rideal could be explained by a combination of these fundamental frequencies, the strong infra-red absorption at 11·90μ coming out exactly as $\nu_1+\nu_2+\nu_3$.

Carbon di-sulphide in the pure state showed the principal line doubled (647 cm^{-1} weak, 656 cm^{-1} strong). The other faint line (795 cm^{-1}) showed a broadening on the long wavelength side. This is quite analogous to the Raman spectrum of gaseous CO_2 obtained by Dickinson, Dillon and Rasetti which consisted of two lines with two weak components. The principal CS_2 line was also found to be slightly shifted to shorter wavelength (about 3 wave nos.) when sulphur was dissolved in it.

1. *Introduction.*

The Raman spectra of simple elements are of the greatest interest, and sulphur is particularly inviting on account of the fact that its infra-red absorption spectrum has been made the subject of extensive study by Taylor and Rideal.[1] The characteristic frequencies could not be determined by the infra-red reflection method since the absorption is not marked and a constant value of about 11% is obtained for reflection.[2] The facts, however, that the molecule of sulphur in the solid state is S_{16} as shown by X-ray analysis,[3] and S_8 in various solvents as shown by the determination of molecular weight, and that it is present as S_2 in the vapour above its boiling point (vapour density measurement) indicate that sulphur should give a complex spectrum with several inactive frequencies due to symmetrical oscillations, which could not therefore appear in the infra-red absorption or reflection. Rhombic sulphur was therefore examined by the author in the same way as described for powdered crystals of inorganic nitrates in a previous paper.[4] A concentrated solution of sulphur in carbon di-sulphide was also examined in order to follow the changes in the Raman lines on dissolution.

2. *Results.*

The intense green line of the mercury arc (5461A) isolated by means of a filter of didymium chloride solution was used as the exciting radiation. Merck's extra pure crystals of sulphur were used as such, and good spectrograms were obtained with two hours' exposure on Ilford soft gradation panchromatic plates (speed, 2000 H & D). The spectrum showed three remarkably strong and sharp Raman lines, the second and third having faint companions (Plate VII). The anti-stokes lines also came out very well, and in a less-exposed plate where the incident line had not broadened out very much, a sharp anti-stokes Raman line corresponding to still more remote infra-red absorption was observed (118μ). A photograph taken with a different spectrograph with a narrower slit showed the stokes Raman line clearly, which agreed in position with the anti-stokes line mentioned previously. The values for the six Raman lines are tabulated below :

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[1] Taylor and Rideal, Proc. Roy. Soc., *115*A, 589 (1927).

[2] Schubert, Dissertation. Breslau, 1916.

[3] Mark and Wigner Z. Phys. Chem., *111*, 398 (1924).

[4] Krishnamurti, Ind. J. Phys., *5*, 1 (1930).

TABLE I.

Exciting line, 5460·74 (18307·5 wave nos.)

Frequency.	Wavelength in I.A.	Wave no. ν	Wave no. diff. $\Delta\nu$.	λ in μ.	Intensity.	Remarks.
ν_0*	5435·6	18392·1	84·6	118·2	Med. Str.	Anti-Stokes line.
ν_1	5506·5	18155·3	152·2	65·7	Strong.	Anti-Stokes line at 5416 A
ν_2	5526·0	18091·3	216·2	46·25	Strong,	Anti-Stokes line at 5397.1A
ν_4	5531·1	18061·8	242·7	41·2	Faint	
ν_5	5593·2	17873·9	433·6	23·06	Faint, diffuse.	
ν_3	5604·6	17837·5	470·0	21·28	Strong	Anti-Stokes (weak) at 5324A.

For examining the solution, carbon di-sulphide proved to be excellent since it could dissolve a large quantity of sulphur, and the two lines due to the solvent were far removed from the Raman lines found in sulphur crystals. A nearly saturated solution at ordinary temperature was examined, and it showed the three prominent Raman lines in approximately the same positions as in the crystal. Careful measurements with reference to the iron arc spectrum and a comparison with that taken for crystalline sulphur with comparable exposure ($\frac{1}{2}$ hour without any filter) showed (1) a disappearance of the anti-stokes of ν_0 in the solution, while the same is present in the crystal, (2) a shift of about 1A to shorter wavelength of ν_1, no measurable change in ν_2 and a shift of about 1A towards longer wavelengths in ν_3. The frequencies for both solution and crystal are set forth below :

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* Stokes' line observed with a different spectrograph at 5485·5 A. This corresponds to infra-red wavelength of 121μ. It was also found with a Hilger 2-prism spectrograph.

TABLE II.

	Crystals.		Solution.	
	$\Delta\nu$.	λ in μ.	$\Delta\nu$.	λ in μ.
ν_0	84·6	118·2	......	......
ν_1	152·2	65·7	148·9	67·2
ν_2	216·2	46·25	216·2	46·25
ν_3	470·0	21·28	473·8	21·11

A very interesting feature is a slight displacement of the strong CS_2 line towards shorter wavelength in the solution. This small shift (Table III) which is of the same order as the shift of the sulphur lines in solution becomes evident when compared with the spectrum for pure CS_2 using iron arc comparison in both cases.

The Raman spectrum of pure CS_2 itself was examined in detail with the result that the two lines, one strong and one weak, recorded by previous observers[5] were found to be double. The strong line had a companion of shorter wavelength, while the weak line showed a broadening to the long wavelength

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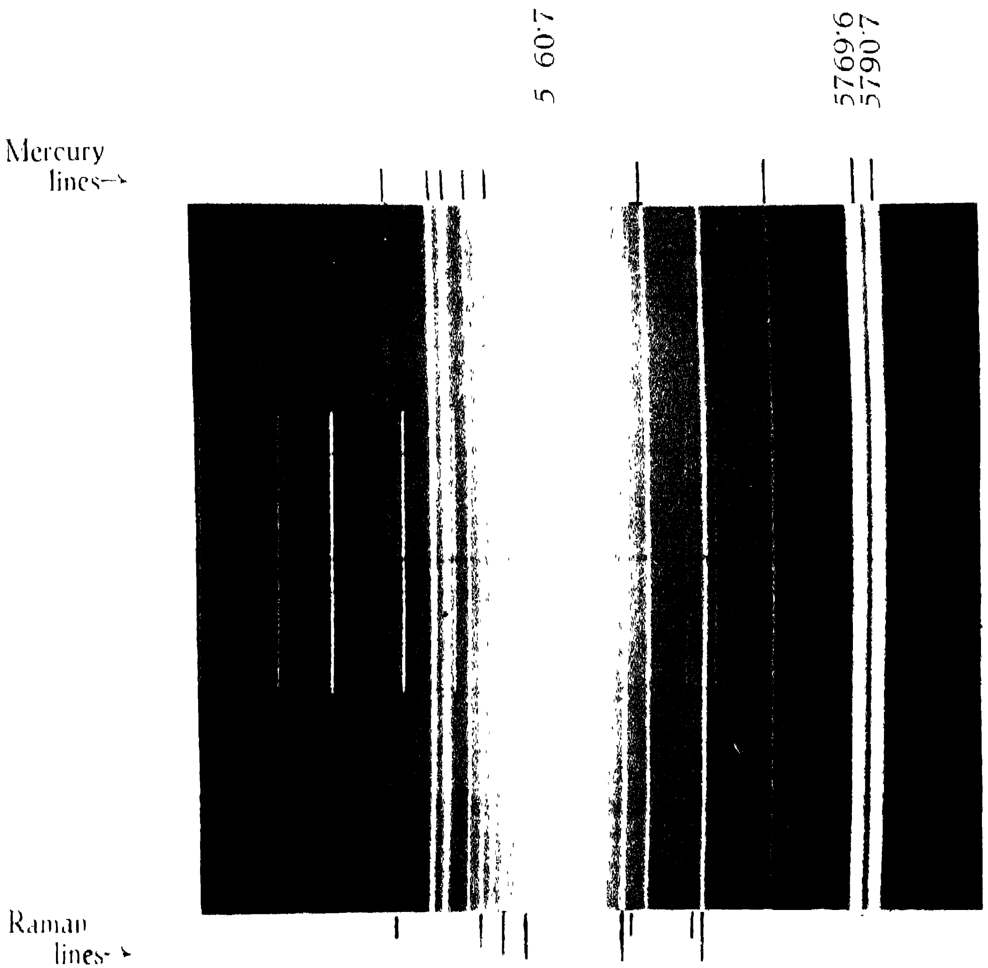
[5] Petrikaln and Hochberg, Z. phys. chem., *3*, 217, (1929).
Ganesan and Venkateswaran, Nature, *124*, 57 (1929).
Schaefer, Matossi and Aderhold, Phys. Z., *30*, 581 (1929).

KRISHNAMURT

PLATE VII



Raman Spectrum of Sulphur.

side which was due to a faint, broad companion barely resolved. On account of its diffuseness it was not found possible to measure this component.

TABLE III.

Exciting line 4358·34 (22938·1)

Substance.	Wave-length in I.A.	Wave no. ν	$\Delta\nu$.	λ in μ.	Intensity.	λ in μ P & H.	λ in μ G & V.	λ in μ S.M.&A.
Carbon di-sulphide	4484·87	22291·0	647·1	15·45	Faint, broad	......	......	...
	4486·56	22282·6	655·5	15·26	Strong, sharp.	15·20	15·27	15·16
	4514·82	22143·1	795·0	12·58	Med Str. broad	12·58	12·50	12·4
Sulphur in carbon di-sulphide	4484·57	22292·4	645·7	15·49	Faint, broad.			
	4486·05	22285·1	653·0	15·31	Strong, sharp.			

The analogy between the CS_2 lines and those of CO_2 gas studied by Dickinson, Dillon and Rasetti[6] is now clear. Each of the two lines has a component, but while the faint CO_2 lines are sharp, the corresponding CS_2 lines are diffuse.

Schaefer, Matossi and Aderhold have reported a faint line in CS_2 (11·8μ) excited by the 4046 line. In the present investigation, a faint line in a similar position could be attributed to the 15·3μ frequency excited by the 4078 line. This is supported by the fact that there is no line at 11·8μ excited by the 4358 line. Hence it is quite evident that the Raman lines in CS_2 do not find any counterpart in infra-red measurements.

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[6] Dickinson, Dillon and Rasetti, Phys. Rev., 34, 582 (1929).

3. *Discussion of Results.*

It will be seen from Table I that the characteristic frequencies correspond to absorptions in the remote infra-red. Hence the absorption maxima found by Coblentz, Schubert and by Taylor and Rideal at 7·76, 10·73 and 11·90μ for rhombic sulphur at ordinary temperature could only be combinations of the fundamental Raman frequencies. Table IV gives a scheme in which the strong frequencies ν_1, ν_2 and ν_3 are mainly involved.*

TABLE IV.

Combination.	ν in wave nos.	Wavelength in μ.	Infra-red absorption (T & R).
$\nu_1 + \nu_2 + \nu_3$	838·4	11·93	11·90
$\nu_2 + \nu_3 + \nu_4$	928·9	10·76	10·73
$2\nu_3$	940·0	10·64	
$\nu_1 + \nu_2 + \nu_5 + \nu_3$	1272·0	7·86	7·76
$\nu_1 + \nu_2 + 2\nu_3$	1308·4	7·64	
$\nu_2 + \nu_3$	686·2	14·57	14·6

The 11·90μ absorption is strongest in the crystal, and is the simplest combination of the three strongest Raman frequencies which appear also in the solution. The agreement between the calculated and observed values is very good. For the other two (10·73 and 7·76μ) an average of two combinations is probable. A fourth infra-red maximum at about 14·6μ shown in Taylor and Rideal's curve could also be explained on the combination basis. The infra-red measurements stop with about 15μ so that other possible combinations corresponding to longer wavelengths cannot at present be compared, but so far as existing data are concerned, the agreement between the two is excellent. This is quite similar to the explanation advanced by Schaefer[7] for the infra-red maxima in calcite by using four fundamental frequencies, and supports the essential correctness of his point of view.

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* Other possible combinations, *e.g.*, $\nu_1 + \nu_3 + \nu_4 + \nu_5$ (7·70μ), $\nu_3 + \nu_5$ (11·07μ) and $\nu_1 + \nu_3 + \nu_4$ (11.56μ) can be mentioned. The last two appear as low maxima in Taylor and Rideal's curve for rhombic sulphur.

We now come to consider the Raman frequencies of sulphur when dissolved in CS_2. The disappearance of the 118μ line is remarkable. This can be understood when we consider the state of aggregation of the molecules in the solution and in the crystal. In the latter it is present as S_{16} and in solution as S_8. Hence the additional frequency ν_0 found in the crystal should be due to the S_{16} group not present in the solution. Since the line is fairly strong and comparable with the other three lines, it may be due to a symmetrical oscillation of the S_{16} group in the crystal. This incidentally throws some light on the origin of the three strong lines common to the crystal and solution. Table V shows the probable origin of the lines.

TABLE V.

Frequency	ν_0	ν_1	ν_2	ν_3
Oscillator	S_{16}	S_8	S_4	S_2

The view was advanced by Taylor and Rideal that in sulphur crystal eight S_2 molecules are present, each occupying a corner of a cube. The fact that each of ν_1, ν_2 and ν_3 is not exactly double the preceding shows that the frequencies do not change in proportion to the increasing mass of the oscillator. But the fact that ν_1 is roughly $2\nu_0$ and ν_3 is roughly $2\nu_2$ is however probably significant.

Finally, it should be mentioned that the frequency obtained by Lindemann's formula (wavelength between 70 and 100μ) does not agree with any of the sulphur frequencies taken singly. If an average value is to be taken, then ν_0 could not be omitted since it is the only one having a smaller frequency than the one calculated from the formula.

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[7] Schaefer and Matossi, Das Ultrarote Spektrum, p. 345 (J. Springer, 1930).

4. *Conclusion.*

This investigation proves the values of the Raman method in determining the fundamental frequencies of the molecules or molecular complexes where infra-red measurements fail to give much information. The Raman spectrum of sulphur solution clearly shows that complex molecules are also present in the solution and this is supported by other methods. The Raman spectrum of sulphur vapour would be very interesting since it is then present as S_2. The polarisation of the Raman lines in the crystal and in solution will also elucidate the origin and nature of the oscillations, and work on these lines is in progress.

The first photograph with sulphur crystals was taken on the 27th March, 1930. The author has much pleasure in thanking Professor Sir C. V. Raman, F.R.S., for his encouragement and guidance during the course of this work.

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Raman Spectra of Crystalline Inorganic Chlorides.

BY

P. KRISHNAMURTI.

(Plate VIII)

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ABSTRACT.

Numerous inorganic halides have now been examined in the form of crystalline powders using the same method as for the nitrates (*Nature*, March 22nd, 1930). Mercuric and mercurous chlorides showed remarkably intense and sharp lines. ($HgCl_2$, 312 cm^{-1} strong, 381 weak; Hg_2Cl_2, 167 and 275 strong, 295 and 320 weak). Linear models are postulated for the molecules of these two chlorides. The Raman spectrum of $HgCl_2$ shows a strong resemblance to that of CO_2 and of CS_2. A saturated solution of $HgCl_2$ in methyl alcohol showed a distinct broadening of the principal line (312 cm^{-1}).

Among the other chlorides, $ZnCl_2$ showed one faint line and CdI_2 three faint lines. A triangular model is indicated for these two substances. $SbCl_3$ and $BiCl_3$ each gave four sharp well-resolved lines shifted in position and much sharper than those recorded for liquid $SbCl_3$ and conc. solution of $BiCl_3$ by Daure. PCl_5 showed four Raman lines, but all the other chlorides examined, *viz.*, those of Li, NH_4, Mg, Ba, Cu (ic), Ag, Cd, Sn (ous) and Th as well as KI and PbI_2 did not show any lines, similar negative results having been recorded for NaCl, KCl, CaF_2 and NaF by Schaefer.

From the above observations the conclusion is arrived at, that covalent bonds are necessary for the production of the Raman effect, the magnitude of which could be determined directly from the known data on the conductivity of the molten chlorides, and less directly from crystal structure data, volatility, solubility and formation of volatile organic derivatives. Compounds where electrovalent linkages only are present fail to show the effect.

1. *Introduction.*

In a recent communication to Nature,[1] the present author has shown the possibility of photographing the complete Raman spectrum of substances in the form of coarse powders or crystalline aggregates. A large number of inorganic nitrates were examined in this way with satisfactory results.[2] This method has now been extended to a study of the inorganic halides, especially the chlorides, in view of the simplicity of their structure. There is, however, another unique interest attaching to this problem. Nearly every experimenter on the Raman effect has examined rock-salt for the rest-strahlen frequency recorded by the infra-red spectra, with decidedly negative results. Prof. Cl. Schaefer finds no lines even with various other cubic crystals,[3] *e.g.*, NaF, LiF, CaF_2 and KCl. On the other hand, the early work of Dr. P. Daure has shown that the chlorides of many non-metals, metalloids and a few metals, *viz.*, of C, Si, Ti, Sn, P, As, Sb and Bi show the Raman spectra in a marked manner. [4] The question naturally arises as to why the effect should appear very prominently in some cases, less so in some others and completely disappear in several other halides. The present investigation on several inorganic chlorides in the solid state was started with a view to provide a satisfactory explanation for these observed phenomena.

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[1] Nature, *125*, 463 (1930).
[2] Ind. J. Phys., *5*, 1 (1930).
[3] Schaefer, C. f. Phys., *54*, 153 (1929).
[4] Daure, Compt. Rend., *187*, 940 (1928).

2. *Experimental Results.*

The same apparatus and procedure were employed as in the previous work on the inorganic nitrates. The mercury arc cooled by a slow current of air was placed close to the triangular cell containing the substance. The scattered light from the side of the cell was concentrated on the slit of the spectrograph by a system of lenses. A Fuess glass prism instrument of high dispersion was used, and exposures ranging from 1-2 hours on backed Ilford Isozenith plates were sufficient to bring out all the Raman lines. The following substances mostly of Kahlbaum and Merck were examined as such, *viz.*, chlorides of Li, Mg, NH_4, Ag, Au, Cu (ic), Ba, Zn, Cd, Hg (ous), Hg (ic), Sn (ous), Th, P, Sb, Bi; also KI, $CdBr_2$, PbI_2 and CdI_2. Antimony and bismuth trichlorides and phosphorus pentachloride gave well-resolved lines. Exceptionally sharp and strong lines were observed with mercuric and mercurous chlorides, with intense anti-stokes components. With zinc chloride one faint line was observed, while with cadmium iodide and gold chloride (examined with 5461 green line of mercury) the Raman lines were feebler still. No lines were given by all the remaining halides. Table I summarises the results obtained with $HgCl_2$, Hg_2Cl_2, $ZnCl_2$, CdI_2,$SbCl_3$, $BiCl_3$ and PCl_5. An iron arc comparison spectrum was photographed on each plate, and the wavelengths calculated by linear interpolation from the nearest known iron lines.

TABLE I.

Raman Lines.

Substance.	Exciting line. λ in I. A.	Wave No.	$\Delta\nu$	λ in μ.	Intensity.
$HgCl_2$ (Mercuric chloride.	4358·34	(1) 22625·8	312·3	32·02	Strong.
		(2) 22556·9	381·2	26·23	Weak.
		23252	314	Anti-Stokes.	
Hg_2Cl_2 (Mercurous chloride).	4358·34	(1) 22771·4	166·7	60·0	Very strong.
		(2) 22663·5	274·6	36·42	Strong.
		(3) 22643·0	295·1	33·89	Weak.
		(4) 22618·1	320·0	31·25	Very weak.
		23102	164	Anti-Stokes	
		23208	270	,,	
$ZnCl_2$ (Zinc chloride.)	4358·34	(1) 22704·4	233·7	42·8	Weak.
CdI_2 (Cadmium Iodide).	5460·74	(1) 18202·3	105·2	95·1	,,
		(2) 17962·5	345·0	29·0	,,
		(3) 17912·3	395·2	25·3	,,
$SbCl_3$ (Antimony Trichloride).	4358·34	(1) 22792·3	145·8	68·6	,,
		(2) 22771·9	166·2	60·2	Medium.
		(3) 22626·1	312·0	32·05	,,
		(4) 22600·6	337·5	29·63	Strong.
$BiCl_3$ (Bismuth Trichloride).	4358·34	(1) 22785·1	153·0	65·4	Very weak.
		(2) 22769·0	169·1	59·1	Weak.
		(3) 22696·2	241·9	41·3	,,
		(4) 22649·9	288·2	34·7	,,
PCl_5 (Phosphorus Pentachloride).	5460·74	(1) 18059·6	247·9	40·3	,,
		(2) 17951·3	356·2	28·1	Medium.
		(3) 17902·7	404·8	24·7	Very weak.
		(4) 17857·9	449·6	22·2	Weak.

3. *Discussion of Results.*

Mercuric Chloride.—It can be seen from Table I that this substance gives rise to one very strong line with a faint companion on the long wavelength side (312 and 381 cm^{-1} respectively). The spectrum is quite analogous to that observed with liquid CS_2 as well as gaseous CO_2, both of which show two lines.[5, 6] In the two latter substances, the Raman lines do not correspond to any of the known infra-red absorption bands, and hence are probably inactive frequencies analogous to the 9·5 μ frequency of the NO_3 ion in the nitrates. The absence of any permanent electric moment in CO_2 and CS_2 taken together with other evidence[7] strongly supports the linear symmetrical rod type of molecule for CO_2 suggested by Eucken.[8] The value for the inactive frequency calculated on this basis agrees very well with that of the observed Raman line. The essential similarity between the Raman spectra of CO_2, CS_2 and $HgCl_2$ strongly suggests a linear model for the $HgCl_2$ molecule, the Raman frequency $\Delta\nu = 312\ cm^{-1}$ representing the symmetrical vibration of the chlorine atoms towards and away from the central atom. (*cf.* $CO_2 = 1284$ and $CS_2 = 655\ cm^{-1}$).

We have still to explain the presence of the weak companion of the prominent Raman line. In $HgCl_2$, its value is $\Delta\nu = 381\ cm^{-1}$, in CS_2 it is 795 and in CO_2 1392 $cm.^{-1}$ It seems very probable that in all these cases we are dealing with a type of oscillation not contemplated by Eucken. It may arise from the oscillation of one of the chlorine atoms against the remaining group (Hg Cl) as a whole, the latter being supposed to be at rest. Similarly, the faint line in CS_2

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[5] Petrikaln and Hochberg; Z. Phys. Chem., 3, 217 (1929).

Rasetti, Nature, 123, 205 (1929).

[7] Rawlins, Trans. Farad. Soc., 25, 925 (1929).

Eucken, Z. f. Phys., 37, 714 (1926).

and in CO_2 may be due to *S—CS and O—CO oscillations* respectively. As the occurrence of this type of oscillation is very limited, the corresponding Raman line is very feeble. It bears a certain analogy to "predissociation" of molecules [9] described by V. Henri, and is supported by chemical evidence. We know that at high temperatures as well as under the influence of light of short wavelength CO_2 breaks up into CO and O, CS_2 loses S and Hg Cl_2 is converted into Hg_2 Cl_2. [10]

A very concentrated solution of mercuric chloride (about 40%) in methyl alcohol was also examined. The strong $HgCl_2$ line occurred practically in the same position as in the crystals, but a considerable broadening was quite evident. A similar broadening of the inactive frequency of the NO_3 ion was observed in the concentrated aqueous solution of lithium nitrate examined previously. [11] It seems probable that the symmetrical broadening observed in the solutions, and in some cases when passing from the solid to the liquid state is due to the increased rotational freedom of the molecules in the molten and dissolved states. These points will be discussed in detail in a separate paper to be published shortly.

Incidentally it may be pointed out that by analogy with CO_2, $HgCl_2$ also could be expected to possess a molecular lattice. The linear symmetrical model further indicates absence of any permanent electric moment, and hence the molecule should be non-polar.

Mercurous chloride (calomel).—The Raman spectrum of this substance consists of a very strong line (167 cm^{-1}) and a strong somewhat broad line (275) with two faint companions (295 and 320 cm^{-1}). It is obvious from the number of lines present that a simple formula like HgCl does not correctly represent mercurous chloride. *This is in harmony* with chemical evidence and strongly supported by crystal structure data. The latter points to a molecular lattice of Hg_2Cl_2, the length of the molecule being parallel to the *C*—axis.[12] Hence a linear symmetrical model Cl-Hg-Hg-Cl is indicated for this substance, as for $HgCl_2$. The strong line (275 cm^{-1}) corresponds to the symmetrical movement of the chlorine atoms towards and away from the central Hg_2 group. The slower oscillation in this case as compared to $HgCl_2$ (312 cm^{-1}) can be explained as due to the greater heaviness of the central group (Hg_2). Its faint companion (295 cm^{-1}) corresponds probably to the Cl—Hg_2Cl oscillation. The origin ɟo the still fainter line (320 cm^{-1}) cannot for the present be decided upon.

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[9] V. Henri, Nature, Dec. 20, 1924.

[10] Plotnikow, Kurzer Leitfaden der Photochemie (G. Thieme, 1928), pp. 48, 114 and 115.

[11] Krishnamurti Ind. J. Phys., 5, 1 (1930).

It should be remarked here that when mercurous chloride is exposed to the light of the mercury arc, the surface layer gets blackened on account of photochemical decomposition : $Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$. The possibility of formation of sufficient $HgCl_2$ in the interior layers is however remote, and hence the faint line (320 cm^{-1}) may not be the $HgCl_2$ line (312 cm^{-1}), though the two frequency shifts lie very near together.

We have now to account for the very strong line ($\Delta\nu = 167$ cm^{-1}). Its strength indicates it as one of the inactive frequencies. The only possible way in agreement with the linear model postulated above for Hg_2 Cl_2 is to assign it to the Cl Hg—HgCl oscillation.

On the basis of the above assumptions, if ν_1 represents the symmetrical oscillation of the chlorine atoms and ν_2 of the Hg atoms, a new combination frequency could be expected $\nu_1 - \nu_2$. This comes out as 108 cm^{-1} or 93 μ agreeing approximately with the rest-strahlen frequency for Hg_2Cl_2

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[12] Hylleraas, Phys. Zeit., 26, 811 (1925).

which is about 98μ. It is of course possible that this is only some chance coincidence since we usually regard the reststrahlen frequency as a fundamental one.

Zinc chloride.—The anhydrous chloride was enclosed in an air-tight cell during the exposure. A single faint line (about 234 cm^{-1}) appeared, with indications of two more lines which, however, were rendered doubtful by the presence of diffraction lines consequent upon intense exposure of the incident lines. It is very likely that it is not the inactive frequency and hence an isosceles triangular model for this substance is indicated.

Cadmium iodide.—The substance investigated consisted of thin flakes. The surface layer got coloured during the exposure due to photochemical decomposition. Three Raman lines excited by the Hg green line 5461, all very weak, were observed. The Raman line (105 cm^{-1}) is probably the analogue of the $ZnCl_2$ line (234 cm^{-1}), the shift to shorter wavelengths in the former being due to the greater mass of I_2 as compared with Cl_2. The same isosceles triangular model will account for the three frequencies observed. This substance is interesting because no effect could be observed in the chloride and bromide. It further crystallises in the characteristic 'layer lattice' intermediate between the molecular and ionic lattices.

Antimony and Bismuth Trichlorides.—$SbCl_3$ has been examined in the liquid state (at about 100°C) by Daure[13] who found two doublets present. He has also examined $BiCl_3$ in a solution of conc. HCl. The relative intensities of the lines as well as their positions in the crystals differ very much from the values of Daure as the following table will show :

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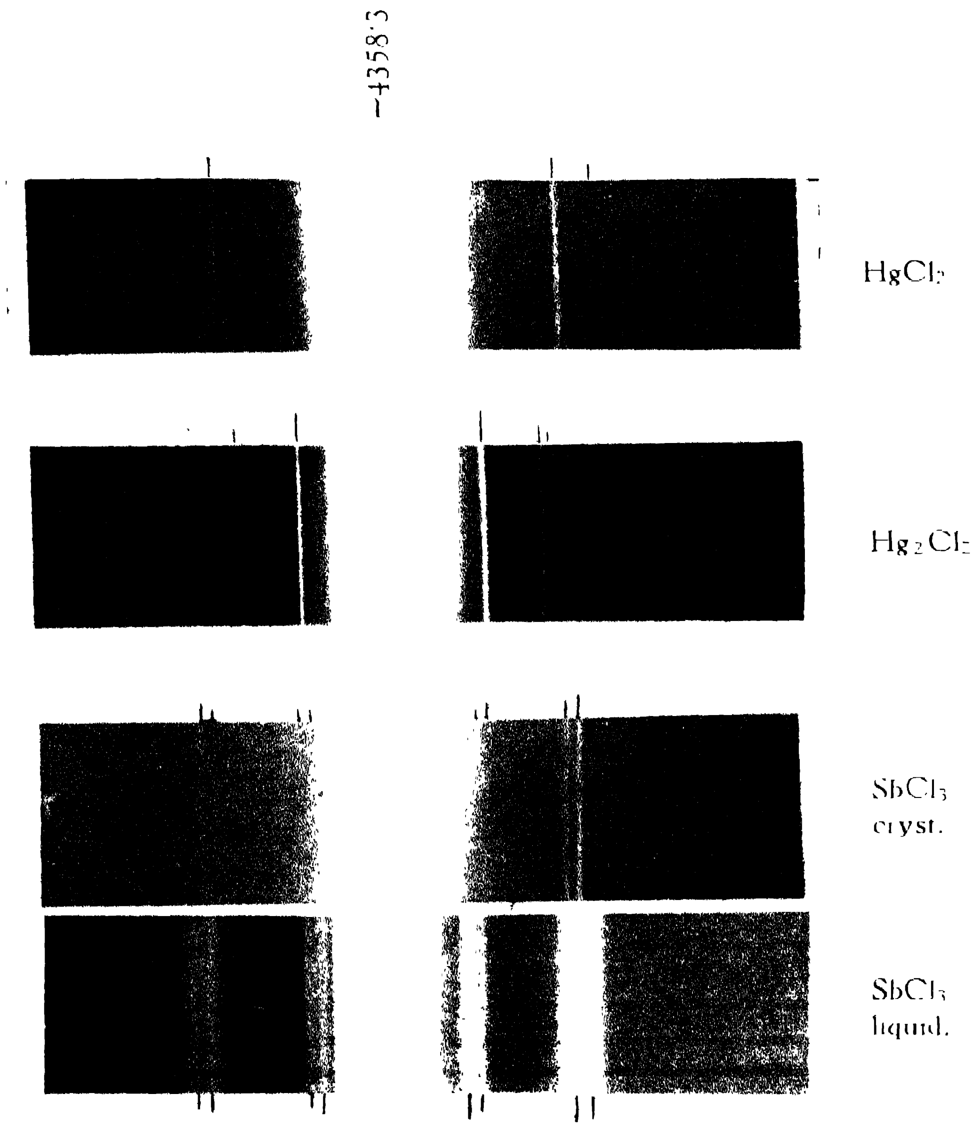
[13] Daure, *loc cit.*



Raman Spectra

TABLE II.

	$SbCl_3$.		$BiCl_3$.	
	Crystals $\Delta\nu$.	Liquid at 100°C (Daure).	Crystals $\Delta\nu$.	Conc. HCl Soln. (Daure).
(1)	146	130	153	110
(2)	166	155	169	—
(3)	312	320	242	240
(4)	338	360	288	290

It will be seen that with $SbCl_3$ crystals the first pair of lines has shifted towards longer wavelengths and the second pair to shorter. The same phenomonon could be noticed in $BiCl_3$ with the first pair of lines.* Further, the crystal lines are considerably sharper. The present author has considered the question of the change from the solid to the liquid state in the case of benzophenone.[14] A broadening of the line due to the ketonic group together with its shift towards longer wavelengths takes place on melting. Hence the polar bonds seem to be most influenced by the change of state, and this conclusion is confirmed by the results with antimony and bismuth chlorides which we know are polar. A fuller treatment of the change in state and how far it influences the Raman spectra of polar and non-polar compounds both organic and inorganic is reserved for a future communication.

Phosphorus Pentachloride.—This substance on account of its very reactive nature was examined in an air-tight container. Since it was coloured yellow and absorbed the blue line, the green mercury line was used as the exciting radiation. Four lines were found, but there were indications of a few more lines closer to the incident line. Until all the possible lines have been isolated it is difficult to picture any model for the PCl_5 molecule. It may, however be pointed out here that none of the lines conicide with those found for PCl_3 by Daure.

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* This, however, is not certain since the lines were very faint and diffraction effects were present in that region.

[14] Krishnamurti, Nature, *loc. cit.*

4. *Raman Effect and the Electronic Theory of Valency.*

It will be useful at this stage to classify the halides under three different groups :

(1) Those that show strong Raman lines, *viz.*, chlorides of Hg (ous) Hg (ic), P, As, Sb, C, Si, Ti, Sn and of hydrogen.

(2) Those that show faint Raman lines, *viz.*, $BiCl_3$ $ZnCl_2$, CdI_2 and $Aucl_3$.

(3) Those that show no lines at all, *viz.*, chlorides of Na, K, NH_4, Ba, Ag, Cu(ic), Cd, Mg, Sn(ous), Th as well as $CdBr_2$, PbI_2, KI, LiF, NaF and CaF_2. A consideration of the properties which the substances in any one group possess in common will enable us to understand the exact significance of the appearance or non-appearance of the Raman spectra.

Electrovalency and Covalency.—It will be seen from the above classification that the chlorides of the strongly electro positive elements do not show the effect while the chlorides of the non-metals and metalloids show it very well. A further distinction between the groups could be effected by finding out whether the union between any atom and chlorine is of the electrovalent (where electron transfer is complete) or covalent type[15] (where there is electron sharing). Since the former type of compounds are completely ionised while the latter are non-ionised, the obvious test for distinguishing between the two types is by means of their conductivity. In the case of most of the inorganic chlorides, we have the data of Biltz and his co-workers on their conductivity just above their melting points.[16] The following table gives the specific conductivities of the various chlorides in reciprocal ohms at the specified temperature. They are arranged in the decreasing order of their conductivity :

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[15] Sidgwick, Electronic Theory of Valency (Oxford, 1927).

TABLE III.

Chloride of.	Temp. in °C.	Eq. conductivity.	Chloride of.	Temp. in °C.	Eq. Conductivity.
Li	613	5·85	In^{III}	586	0·43
Ag	455	3·77	Bi^{III}	227	0·38
Na	800	3·54	Yt	700	0·37
Cu^{I}	422	3·25	U^{IV}	570	0·34
K	768	2·12	In^{II}	235	0·23
Ba	960	1·95	Te^{IV}	236	0·115
Ca	774	1·93	Te^{II}	206	0·042
Sr	873	1·90	Zn	318	8×10^{-4}
Cd	564	1·88	Hg^{II}	277	$0{\cdot}8 \times 10^{-4}$
Rb	714	1·16	Mo^{V}	216	$1{\cdot}8 \times 10^{-6}$
Pb^{II}	498	1·44	W^{VI}	280	$1{\cdot}98 \times 10^{-6}$
La	860	1·12	As^{II}	0	$1{\cdot}24 \times 10^{-6}$
Cs	645	1·11	Sb^{III}	73	$0{\cdot}85 \times 10^{-6}$
Tl^{I}	430	1·09	Pb^{IV}	0	$0{\cdot}8 \times 10^{-6}$
Mg	712	1·02	W^{V}	250	$0{\cdot}67 \times 10^{-6}$
Pr	824	0·82	Al^{III}	194	$0{\cdot}45 \times 10^{-6}$
Sn^{II}	245	0·78	Ta^{V}	230	$0{\cdot}3 \times 10^{-6}$
Nd	775	0·63	Nb^{V}	220	$0{\cdot}22 \times 10^{-6}$
Th	765	0·56	Se	18	$0{\cdot}2 - 10^{-6}$
Sc	940	0·50			

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[16] Gmelin's Handbuch der Anorg. Chem. (Verlag Chemie, Berlin, 1927).

In addition to the above, we have other chlorides enumerated below for which exact data are not available.

TABLE IV.

Good-conductors.	Non-conductors.	
$GaCl_2$	BCl_3	VCl_4
$CrCl_2$	CCl_4	$SbCl_5$
$InCl_3$	$SiCl_4$	S_2Cl_2
$MnCl_2$	$TiCl_4$	ICl
$FeCl_2$	$GeCl_4$	ICl_3
$CoCl_2$	$SnCl_4$	
$NiCl_2$	PCl_3	
$PdCl_2$	PCl_5	

It will be seen from tables III and IV that only non-conductors and very feeble conductors show the Raman effect while good conductors do not show the effect at all. We know also that gaseous[17] and liquid HCl[18] which are non-conductors show the effect which however disappears once it is dissolved in water where it ionises and becomes an excellent conductor. The case of mercuric chloride is indeed very striking. The conductivity of the molten substance is very low and even in aqueous solutions it is but very little ionised. In fact as Sidgwick remarks,[19] "the tendency of mercury to assume the convalent form is quite exceptional, and must be due in part to causes outside the Fajans theory." We also find that the Raman spectra of the mercury chlorides are surprisingly intense. The entire host of organic compounds characterised by covalent linkages show the effect without any exception. These facts are essentially in agreement with the view put forward in this paper that the strength of the covalent linkage between the atoms decides the presence or absence of the Raman lines. The difference between two chlorides of the same metal, *viz.*, $SnCl_2$ and $SnCl_4$, the former a good conductor in the molten state and the later a non-conductor is shown by the absence of Raman lines in the one and by their presence in the other.

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[17] Nature, *123*, 279 (1929).

[18] Salant and Sandow, Phys. Rev., *33*, 1096 (1929).

[19] Sidgwick, *loc. cit.*, p. 107.

Apart from the conductivity in the molten state, conductivity in aqueous solutions, wherever it is possible, will give us an idea of the strength of the covalency bonds. The case of $HgCl_2$ as mentioned before illustrates this point. Progressive ionisation should result in a weakening of the Raman lines, as has indeed been found by Daure with solutions of antimony and bismuth chlorides.

Crystal structure.—As has already been pointed out, the broad division between ionic and molecular lattices finds a counterpart in the Raman spectra, the typical ionic crystals (NaCl, KCl) giving no lines while the typical molecular substances (CCl_4, Hg_2Cl_2) show prominent Raman lines. Substances belonging to the NaCl, CsCl and CaF_2 types are not favourable while the Hg_2 Cl_2 (molecular) type is very favourable for the production of Raman lines, the CdI_2 type (Schichtengitter) being probably the transition stage.

Other Physical Properties.—Chief among these are volatility, power of forming stable organic derivatives and solubility in polar or non-polar solvents which serve to distinguish the electrovalent from the covalent type of linkage. The latter type of compounds as also those which show strong Raman spectra usually possess low melting and boiling points while the others like the alkali halides possess very low volatility. While the latter are freely soluble in water and almost insoluble in benzene, the former compounds dissolve in benzene or other non-hydroxylic solvents with fair readiness. As Sidgwick points out,[20] however, the solubility and volatility may also be lessened by other causes such as polymerisation or association. Typical instances of this kind are the 'giant molecules' of diamond or silicon carbide, in which the whole crystal is one great molecule with all its atoms held together by covalent links. They possess no vapour pressure or solubility, and their melting and boiling points are very high. Their non-polar character could be judged only from their crystal structure.

The formation of alkyl or aryl derivatives is very characteristic of certain metals. Of these mercury is very prominent, and as Sidgwick says,[21] "Far more organic compounds are known of mercury than of all the other metals together." Lead and tin in the tetravalent condition, cadmium, germanium, zinc, boron, silicon, phosphorus, arsenic, antimony and bismuth form organic derivatives with great ease, *e.g.*, the alkyls, most of which are stable and possess low boiling points. There is no doubt that in these compounds covalent bonds are present. It is interesting to note that compounds of divalent lead and tin are comparatively rare. The presence of covalent bonds and the existence of Raman lines in the halides seem to go hand in hand with the power of forming stable organic compounds.

Raman Effect and the Periodic System.—Since only the valency electrons seem to be primarily concerned in the Raman effect, a consideration of the position occupied by the particular element in the periodic table would be of interest. The nature of the binding between the atoms in the halides from the point of view of their physical properties, *viz.*, their volatility, type of crystal lattice and electrical conductivity has been examined by Grimm and Sommerfeld, Goldschmidt

Sidgwick, *loc. cit.*, p. 89 and 264.

and by Bitz and Klemm. The following classification from a paper by Grimm [22] shows the division between the two types of halides:

TABLE V.

Fluorides.				Chlorides.			
LiF	BeF_2	*BF_3*	*CF_4*	$LiCl$	*$BeCl_2$*	*BCl_3*	*CCl_4*
NaF	MgF_2	AlF_3	*SiF_4*	$NaCl$	$MgCl_2$	*$AlCl_3$*	*$SiCl_4$*
KF	CaF_2	ScF_3	*TiF_4*	KCl	$CaCl_2$	$ScCl_3$	*$TiCl_4$*
RbF	SrF_2	YF_3	*ZrF_4*	$RbCl$	$SrCl_2$	YCl_3	$ZrCl_4$
CsF	BaF_2	LaF_3	CeF_4	$CsCl$	$BaCl_2$	$LaCl_3$	$CeCl_4$

Substances in italics are of the covalent type. The others are mostly of the electrovalent type.

The conclusion is arrived at that with increasing deforming effect of the cation (with decreasing radius and increasing charge) and also with increasing deformability of the anions (with increasing charge and size), the greater is the possibility of the transformation from the polar to the non-polar type, or, in other words, conversion of the electrovalent into covalent bonds. Hence the Raman effect should show a similar change, and at least among the halides this seems to be supported by the present experiments.

5. *Conclusion.*

It will be seen from the foregoing that the study of Raman spectra of crystals enables us to distinguish easily between the electrovalent and covalent types of linkages in chemical compounds. It gives valuable information about the shape and structure of the molecules in the crystal lattice in agreement with X-ray data. The calculation of the specific heats in the simpler crystals which show the effect is at present being attempted. Further work on the effect of solution and fusion on the Raman spectra of polar and non-polar inorganic and organic compounds is in progress which will throw considerable light on molecular association, rotational-vibrational effects in liquids and related questions.

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[22] Grimm, Naturwiss., *17*, 538 (1929).

I have great pleasure in thanking Prof. Sir C. V. Raman under whose inspiring guidance this work was carried out, for numerous suggestions and advice during its progress.

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10

Interpretation of Raman Spectra: Some Aliphatic Amines and Alcohols.

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Abstract.

The paper describes the results of a study of the Raman effect in three simple aliphatic compounds, *viz.*, methyl, ethyl and triethylamines examined for the first time. Some of the alcohols have also been studied in greater detail and the results included here. Methyl and ethylamines give broad Raman lines corresponding to about 3300 which are attributed to the N—H linkage. This frequency does not appear in triethylamine as may be expected. All the three amines have a frequency of about 1050 in common and this is attributed to the C—N linkage. The methyl alcohol shows three broad bands corresponding to a wave length 3μ excited by the three principal mercury lines 3650, 4046, 4358. In the latter two cases however it is very weak. This band which is evidently analogous to the water band is not observed in the higher alcohols.

The results obtained, together with some of the already available data are discussed in the light of certain characteristic common configurations. It is pointed out that associated with the prominent frequencies hitherto attributed to certain well defined chemical linkages, there are also present other less conspicuous vibrations which may also be regarded as characteristic of the particular configuration. The alcohols and the acids have three well defined frequencies common to all of them having values about 1050, 1250 and 1360. These are attributed to the $-\overset{|}{\underset{|}{C}}-OH$ group. There are however two other frequencies of about 600 and 1700 in the acids which are absent in the alcohols. They are attributed to the

$\overset{\|}{\text{—C—}}$ configuration, the one at 1700 being usually the more prominent of them and hitherto associated with the C=O linkage.

A comparison of the paraffins and their derivatives such as the alcohols nd acids in themselves reveals that a C—C linkage has a frequency of bout 900 which splits into three and more components with increasing omplexity of the carbon chain. A close resemblance is seen to exist etween the oscillation frequencies of a paraffin, the corresponding alcohol nd the acid.

1. *Introduction.*

It is now well known that a study of the Raman spectra eveals the fundamental oscillation frequencies of the various nolecules. There have been recent attempts to associate ertain well defined frequencies with characteristic chemical inkages which have met with fair success. It must however e borne in mind that in such complicated cases, we are dealng with the molecule as a whole, and hence an attempt to solate particular linkages as having unique oscillations is true nly as an approximation. For an exact study, the vibrations f the complete molecule have to be worked out and the haracteristic modes analysed, taking into consideration the nutual influence of all the atoms and the linkages. Such an nalysis is however likely to be complex even in the simplest of the compounds. Hence it may be useful to adopt an intermediate position and recognise the presence in the molecule f characteristic polyatomic groups, each containing several inkages and capable of several different modes of vibration hich may be regarded as approximately characteristic of he group. Such oscillations would naturally include also the rominent frequencies usually regarded as characteristic of articular linkages present in the group. It must however e made clear that such a view is only an attempt to reconile the two widely different conceptions of the moleculeactg as a whole on the one hand, and the component linkages acting independently on the other. In the following sections it will in fact be noticed that the group frequencies are considerably influenced by the surrounding conditions in the molecule.

The present paper consists of the results obtained in a study of some of the early members of the aliphatic amines and a more detailed investigation of some of the alcohols. An attempt to interpret the results on the above basis is made. In all cases, substances supplied by Kahlbaum have been made use of after a further purification by distillation in vacuum; methyl and ethyl amines were however used in unopened sealed bulbs as they have very low boiling points. Ethyl alcohol was dehydrated with anhydrous copper sulphate before distillation. Experimental arrangements were similar to those described in the previous papers. A large two prism glass spectrograph supplied by Adam Hilger and a quartz E_2 have been made use of in the investigation. The results are given in the following tables, in which I stands for the relative intensity of the Raman line, ν the wave number in vacuo and $\Delta\nu$ the frequency shift. Letters *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, and *k* represent the principal mercury lines 3650·1 3654·8, 3663·3, 4046·6, 4077·8, 4339·3, 4347·5, 4358·3 and 5460·7 respectively.

2. *Experimental Results.*

Amines.—Three aliphatic amines have been studied in this paper. The results are given in Tables I to III. The simplest of them, *viz.*, methylamine, reveals four prominent frequencies at 1033, 2870, 2955 and 3301. The frequencies 2870 and 2955 are evidently due to the C – H linkage and 3301 to the N – H linkage. The Raman line arising from this latter frequency is a broad line bearing a close resemblance to the Raman lines of ammonia. Besides there is a weak band shifted by about 500 wave numbers from the 4358 line whose broad and diffuse nature suggests that its origin may be in a group of weakly associated molecules.

Ethylamine, the next member, shows a few more frequencies, the most important one being at 900 which as will be shown in the following discussions, can be attributed to the C—C linkage. In this compound also the Raman line due to the N—H linkage is broad and appears quite prominently although in a slightly shifted position corresponding to a frequency shift of 3320. Such a broad and diffuse nature of the Raman lines associated with this frequency is in some respects analogous to the broad bands appearing in water and other relatively simple compounds like methyl alcohol containing the O—H group and if it is in any way inherent with the particular linkages under consideration is more than what can be said from the available evidence. It is however of interest to note that in these cases where broad bands are present, a hydrogen atom is usually involved in the oscillations. In ethylamine there is a frequency of about 1597 which is probably associated with the N—H linkage besides its usual oscillation 3321, just as the 1450 is attributed to C—H in addition to the prominent band at about 3000.[1]

Contrary to these two cases, the scattered spectrum of triethylamine, does not contain Raman lines corresponding to 3300. This is in accordance with what might be expected since all the hydrogen atoms attached to the nitrogen have been replaced by ethyl groups in this compound.

There is a prominent frequency of about 1050 common to all the three amines which may be attributed to the C—N linkage. It may be noted that a calculation of this frequency on the basis of the formula $\nu=\frac{1}{2\pi}\sqrt{\frac{k}{u}}$ taking the thermal dissociation constant for this linkage as 76 kilo. calories per gm. mol., yields 1000.

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[1] The view that one is a transverse and the other longitudinal oscillation has been expressed by Ellis and others. See Jour. Frank. Inst., Vol. 208, p. 517 (1929).

TABLE I.

Methylamine, CH_3NH_2.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
0	19973	$h-2955$	2	21835	$d-2870$	2	23672	$d-1033$
2*b*	21404	$d-3301$	0	Band*		2	Band*	
2	21755	$d-2950$	2	21905	$h-1033$	0	24434	$a-2955$

$\Delta\nu$:—1033 (2), 2870 (2), 2955 (2), 3301 (2*b*).

* The centre of the band is at λ 4159 and corresponds to the 3μ line (NH) excited by the group of lines λ 3650, 3654 and 3663. There is another feeble band shifted by about 500 wave numbers from λ 4358.

TABLE II.

Ethylamine, $CH_3CH_2NH_2$.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
0	19960	$h-2978$	6	21779	$d-2926$	1*b*	24018	$b-3336$
0	20011	$h-2927$	6	21830	$d-2875$	3*b*	24064	$a-3325$
0	20077	$h-2861$	2	22036	$h-902$	1	24371	$\left.\begin{matrix}c-2919\\b-2983\end{matrix}\right\}$
1	21341	$h-1597$	2	23241	$d-1464$			
2*b*	21388	$d-3317$	1*b*	23427	$e-1089$	1	24413	$a-2976$
1	21486	$h-1452$	2*b*	23609	$d-1096$	1	24466	$a-2923$
1	21571	$e-2945$	2	23807	$d-898$			
0	21646	$e-2870$	0	23905	$d-800$			
6	21734	$d-2971$	2*b*	23976	$c-3314$			

$\Delta\nu$:—800 (0), 900 (2), 1092 (2*b*), 1452 (1), 1597 (1), 2869 (4) 2927 (6), 2974 (6), 3321 (2*b*).

TABLE III.

Triethylamine $(C_2H_5)_3N$.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
0*b*	19978	*h*−2960	1	21826	*d*−2879	0*b*	23791	*d*−914
2	21479	*h*−1459	1b	21884	*h*−1054	0	23958	*d*−747
0	21555	*e*−2961	0	22022	*h*−916	0	24257	*d*−448
0	21635	*h*−1303	0	22185	*h*−753	0	24373	*b*−2981
3	21733	*d*−2972	0*b*	23391	*d*−1314	0	24412	*a*−2977
3	21771	*d*−2934	0*b*	23642	*d*−1063			

$\Delta\nu$:—448 (0), 750 (0), 915 (0), 1058 (1*b*) 1309 (0*b*), 1459 (2), 2879 (1), 2934 (3), 2972 (3).

Alcohols.—The Raman spectrum of methyl alcohol shows, besides the lines given in Table IV, a prominent broad band corresponding to a shift of about 3μ from the 3650 group of mercury lines. The corresponding band arising from 4046 is also seen quite clearly on the plate but is less prominent, whereas the one excited by 4358 is just visible. Tables V to IX contain the results obtained with ethyl, propyl, butyl and isobutyl alcohols and trimethyl carbinol respectively. The last three have been chosen in view of the fact that they are isomeric with one another.

TABLE IV.

Methyl Alcohol, $CH_3.OH$.*

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
1*b*	19996	*h*−2942	1*b*	21718	*h*−1220	0	23344	*d*−1361
2	20105	*h*−2833	8	21760	*d*−2945	0	23474	*d*−1231
5*b*	21470	*h*−1468	10	21870	*d*−2835	5	23670	*d*−1034
0	21527	*g*−1468	5	21904	*h*−1034	4*b*	24403	*b*−2951
1*b*	21568	*h*−1370	0*b*	22161	*h*−777	4*b*	24448	*a*−2941
		c−2948	0*b*	22652	*h*−286	4*b*	24555	*a*−2834
1*b*	21678	*e*−2838	4*b*	23235	*d*−1470			

$\Delta\nu$:—286 (0*b*), 777 0(*b*), 1034 (5), 1225 (0), 1365 (0) 1469 (5*b*), 2835 (8), 2945 (6).

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* Since the paper was sent to the press, a publication by Dadieu and Kohlrausch has appeared (Wien, Berichte, Band 139, p. 177) containing their results for aqueous solutions of methyl and ethyl amines and new measurements for methyl and ethyl alcohols. The former show appreciable differences from those given in the present paper for pure amines in the liquid state. The presence of frequencies 1225 and 1365 in methyl alcohol has been confirmed by us, giving long exposures (see Table IV).

TABLE V.

Ethyl Alcohol, $CH_3.CH_2OH$.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
0	20010	*h*−2928	4	21773	*d*−2932	1	23430	*d*−1275
0	20070	*h*−2868	2*b*	21829	*d*−2876	1*b*	23658	*d*−1047
1	21485	*h*−1453	0	21891	*h*−1047	3	23823	*d*−882
0	21584	*h*−1360	2*s*	22052	*h*−886	2	24419	*a*−2970
0	21660	*h*−1269	0	22488	*h*−450	1	24460	*a*−2929
3*b*	21728	*d*−2977	2	23235	*d*−1470			

$\Delta\nu$:—450 (0), 884 (3), 1047 (0), 1272 (1), 1360 (0), 1461 (2), 2872 (2), 2930 (4), 2973 (2).

TABLE VI.

Propyl Alcohol, $CH_3.CH_2.CH_2OH$.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
1	19996	*h*−2942	2	21879	*h*−1059	4	23848	*d*−857
1	20026	*h*−2912	2	21971	*h*−967	0*b*	23951	*d*−754
1	20074	*h*−2864	2	22050	*h*−888	0*b*	24049	*e*−467
4	21475	*h*−1463	4	22082	*h*−856	1*b*	24248	*d*−457
0	21574	*h*−1364 *e*−2942	1	22483	*h*−455	0	24381	*b*−2973
2	21650	*h*−1288	4*b*	23242	*d*−1462	1	24407	*a*−2972
2	21733	*d*−2972	0 2b	23352 23424	*d*−1353 *d*−1281	0	24460	*a*−2929
4	21765	*d*−2940	3*b*	23644	*d*−1061	0	25931	*a*−1457
8	21798	*d*−2907	2	23736	*d*−969	0	26025	*a*−1364
8	21828	*d*−2877	2	23812	*d*−893	0	26104	*a*−1294

$\Delta\nu$:—456 (1), 754 (0), 857 (4), 890 (2), 968 (2), 1060 (2), 1284 (2), 1364 (0), 1463 (4), 2877 (6), 2910 (6), 2942 (2), 2973 (1).

TABLE VII.

Butyl Alcohol, $CH_3.CH_2.CH_2.CH_2OH$.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
2*b*	21491	*h*−1447	6	21847	*d*−2858	1*b*	23650	*d*−1055
0	21625	*e*−2891	2*b*	21894	*h*−1044	1*b*	23755	*d*−950
3	21654	*e*−2862	2	22125	*h*−813	1	23892	*d*−813
		h−1284	1	22557	*h*−381	0	24393	*b*−2961
3	21754	*d*−2951	2*b*	23267	*d*−1438	1	24425	*a*−2964
4	21783	*d*−2922	2	23418	*d*−1287	1	24459	*a*−2930
5	21813	*d*−2892	0*b*	23590	*d*−1115	1	24490	*a*−2899

$\Delta\nu$:—381 (1), 813 (2), 950 (1*b*), 1050 (2*b*), 1115 (0*b*), 1286 (2), 1442 (2*b*), 2858 (6), 2892 (5), 2922 (4), 2951 (3).

TABLE VIII.

Isobutyl Alcohol, $(CH_3)_2.CH.CH_2OH$.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
5	19978	*h*−2960	10	21833	*d*−2872	0	23458	*d*−1247
5	20070	*h*−2868	0	21892	*h*−1046	1	23577	*d*−1128
4*d*	21480	*h*−1458	3*dv*	21978	*h*−960	0	23658	*d*−1047
2	21557	*g*−1438	0	22032	*g*−963	0	23701	*e*−815
		e−2959	5	22118	*h*−820	2*b*	23744	*d*−961
2	21596	*h*−1342	1	22150	*h*−783	5	23886	*d*−819
2	21643	*e*−2878	2	22442	*h*−496	1	23920	*d*−785
0	21693	*h*−1245	3*d*	23241	*d*−1464	2*d*	24209	*d*−496
10*b*	21742	*d*−2963	1	23364	*d*−1341	4*b*	24422	*a*−2967

$\Delta\nu$:—496 (2), 784 (1), 819 (5), 961 (3*b*), 1047 (0), 1128 (1), 1246 (0), 1342 (2) 1461 (4*d*), 2871 (10), 2962 (10).

TABLE IX.

Trimethyl Carbinol, $(CH_3)_3.COH$.

I	ν	Δν	I	ν	Δν	I	ν	Δν
3	10961	*h*−2997	4	21786	*d*−2919	0	23597	*d*−1108
3	20023	*h*−2915	0	21821	*h*−1117	0	23764	*e*−752
3*b*	21487	*h*−1451	3*b*	22025	*h*−913	2*b*	23792	*d*−913
0*b*	21535	*e*−2981	5*s*	22187	*h*−751	4	23953	*d*−752
0	21596	*e*−2920	0	22593	*h*−345	0	24312	*c*−2978
5	21725	*h*−1213	0	22794	*h*−144	3	24371	*b*−2983
		d−2980	2*b*	23255	*d*−1450	6	24412	*a*−2977
0	21764	*d*−2941	0	23503	*d*−1202	4	24473	*a*−2916

Δν :—144 (0), 345 (0), 751 (5), 913 (3*b*), 1112 (0), 1202 (0), 1450 (3*b*), 2917 (4), 2941 (0), 2986 (5).

3. *Discussion of the Results.*

Alcohols.—A comparison of the results obtained with various alcohols studied in this paper reveals certain interesting features. The following table shows their relationship.

TABLE X.

Comparison of Alcohols.

Methyl alcohol	1034 (5)	1225 (0)	1365 (0)
Ethyl ,,	1047 (0)	1272 (1)	1360 (0)
Propyl ,,	1060 (2)	1284 (2)	1364 (0)
Butyl ,,	1050 (2*b*) *	1286 (2)	......
Isobutyl ,,	1047 (0)	1246 (0)	1342 (2)
Trimethyl Carbinol	......	1202 (0)	......

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* The broad nature of this frequency may be associated with the view that there is one of that magnitude which may as well be attributed to the carbon chain. See Table XII.

Besides the band in the region 2850 to 2970, a frequency at about 1450 is common to all the alcohols and is attributed to the C—H linkage. The table shows all the other lines appearing in methyl alcohol with the exception of two weak and diffuse ones at 286 and 777. The diffuse character of these oscillations suggests that they probably arise from loosely associated molecules. It will be seen that the three frequencies 1034, 1225 and 1365 appearing in the first member of the series are conserved in all the higher members, the actual values varying within narrow limits from compound to compound. Such a result is to be expected in view of the fact that the COH group is present in all of them. Interesting variations can be noticed on an examination of these frequencies. The magnitude as well as the intensity of the one at 1200 increases as we go up the series of normal alcohols. On the contrary, in the isomers, it is less prominent and assumes a lower value than in the corresponding normal alcohols. A comparison of the three isomeric butyl alcohols given in Table X reveals the above features clearly. The frequency at 1030 behaves likewise in that it shows a definite tendency to increase in magnitude in the series of normal alcohols. On the contrary the frequency at 1360 remains practically unaltered. Such variations clearly show that the conception of a group acting as an independent seat of local oscillations is only approximately true and that the neighbouring groups are bound to influence the same.

It must however be noted here that the trimethyl carbinol differs from all the others in the list in many respects in that there is no frequency corresponding to either 1040 or 1360 which are both present in the other alcohols. Such an anomalous character may be associated with the peculiar chemical structure, namely, that the central carbon atom is more or less symmetrically loaded with methyl groups on all sides. A similar phenomenon is observed in propyl and isopropyl chlorides, *viz.*, that a frequency 735 which is quite prominent in the former and other chlorides can only just be detected in the latter.[2]

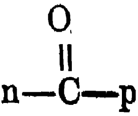
Fatty Acids.—It is interesting to note that precisely the same relationships hold good in the series of fatty acids. Data available are given in Table XI in which frequencies that are usually characteristic of the series alone are included.

TABLE XI.

Comparison of the Acids.

Formic acid	687		1223		1694
Acetic ,,	623	1021	1280	1364	1670
Propionic ,,	608	1033	1275	1365	1662
Butyric ,,	613	1044	1293	1364	1659

Just as in the case of the alcohols there are three frequencies at 1030, 1250 and 1360 conserved throughout the series of compounds and are likewise attributable to the COH group. Their behaviour as we go up the series is in many respects analogous to that encountered in alcohols in that the first two frequencies 1030 and 1250 show a marked increase, whereas the one at 1360 is remarkable in that it shows no variation from compound to compound. Besides, the frequencies appearing in any particular acid have more or less the same values as in the corresponding alcohol.

Unlike the alcohols, however, there are two more frequencies of about 600 and 1700 common to all the acids, a result which may be associated with the configuration  $—\overset{\overset{\displaystyle O}{\|}}{C}—$ present in the acids but absent in the alcohols. This view is supported by the fact that these two frequencies occur in most ketones, aldehydes, esters, etc., although slightly modified.

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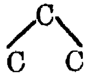
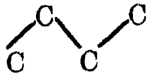
[2] S. Bhagavantam and S. Venkateswaran, Proc. Roy. Soc., Vol. 127, p. 360 (1930).

Carbon Chain.—The transition from the first member to the next of the paraffin series is accompanied by the development of a carbon chain consisting of only two atoms. It is interesting to note that this change results in the production of a new Raman line at 990 in ethane.[3] Similar results are noticed on comparing the Raman spectra of substituted compounds of methane and ethane. On the other hand the higher members show two or more Raman lines in the vicinity of the above oscillation frequency. The following table shows such of the Raman lines having their origin in the carbon chain.

TABLE XII.

Carbon Chain.

	Paraffins.	Alcohols.	Fatcy acids.
C	...	...	...
C–C	990	884	901
	870, 940, 1050	857, 890, 968	770, 854
	...	813, 950, 1050, 1115	778, 869

It is evident from the table that as we go up any particular series, the frequency of the principal oscillation shows a rapid decrease[4] and is accompanied by other components. This may be expected in view of the increasing complexity of the chain. There is also a definite decrease in the value of this frequency as we pass from the hydrocarbons to their corresponding alcohols and acids. This again is in accordance with the fact that in the latter the carbon chain is loaded at one end. In all the three series of compounds, while the second member shows only one line evidently corresponding to the C—C, the third, fourth and fifth members show 3, 4 and more frequencies respectively. The appearance of three oscillations in propane must in some manner be connected with the structure of the chain which is presumably a zig-zag one.[5] Such a structure can no doubt be expected to give three fundamental oscillations but the precise significance of their being so near each other is however not clear. The same chain persists in the derivatives as well and accordingly gives rise to analogous results.

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[3] P. Daure, Rep. of the Faraday Soc. on "Mol. Spectra and Mol. Structure," p. 827 (1929)

[4] See also A. Dadieu and K. W. F. Kohlrausch, Berichte, Vol. 63, p. 251 (1930).

The C—H band.—A comparison of the frequencies characteristic of the C—H linkage in the alcohols studied in this paper reveals interesting features. In methyl alcohol, the band consists of only two components, whereas in ethyl alcohol, it has three. In the normal butyl alcohol the band is distinctly resolved into four components while in isobutyl alcohol, it consists of only two prominent lines with a continuous spectrum in between. In trimethyl carbinol there is present however a feeble line between two strong components which constitute the band. Such a relatively simple structure for the band presented by the earlier members and its development as we proceed up the series is also to be seen clearly in other compounds. In this connection it is thought of interest to examine the behaviour of this band in various simple compounds. The following table shows the values of the components of the band appearing in some simple compounds.

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[5] See 'Roy. Soc. Proc.,' Vol. 120, p. 437 (1928), and other subsequent papers by A. Muller.

TABLE XIII.

C—H BAND.

Methane ...	M.S.W.			2910		2953	2999	3023	3047	3071			
Ethane ...	D		2890			2950							
Butane ...	D		2870	2910		2950							
Pentane ...	G.V.	2854	2876	2906	2937	2964							
Heptane ...	G.V.	2853	2872	2912	2931	2963							
Octane ...	G.V.	2853	2873	2907	2936	2964							
Methyl alcohol ...		2835			2945								
Methylamine ..			2870			2955							
Nitromethane ...	G.V.					2961			3042				
Methylene chloride ...	B.V.				2936		2988						
Chloroform ...	G.V.							3020					
Ethylene ...	D-D.R.		2880					3019					
Acetylene ...	D												3320
Cyclohexane ...	G.V.	2853	2890	2921	2935								
Benzene ...	S				2947				3047	3061	3163	3185	

M. S. W :—J. C. McLennan, H. D. Smith and J. O. Wilhelm.
D. :—P. Daure.
G. V. :—A. S. Ganesan and S. Venkateswaran.
B. V. :—S. Bhagavantam and S. Venkateswaran.
D. D. R. :—R. G. Dickinson, R. T. Dillon and F. Rasetti.
S. :—Jonas Soderquist.

The components of the band lie in the region 2850 to 3320. In methane, the simplest of the compounds, the band consists of one strong line at 2910 accompanied by five other feeble components. On the other hand the substituted compounds of methane show a band consisting of only one or two components as will be seen from the table given above (methyl alcohol, methylamine, nitromethane, etc.). In the higher members such as pentane, heptane, etc., and their derivatives the band consists of several more or less equally spaced lines all confined to the region 2850 to 2970, whereas in benzene and other aromatic compounds not shown in the table, the most prominent components are in the region beyond 3050. In the intermediate region extending from 2970 to 3050, the components do not generally occur except when there is an unsaturated bond as in ethylene [6] or in certain compounds like chloroform and bromoform. In acety lene which is more unsaturated than ethylene, the band shifts further up giving the largest value, *viz.*, 3320.

The fact however that in methane there do occur components although very weak in the intermediate region 2970 to 3050 and beyond suggests that all these components are characteristic of the hydrogen atom, the structure of the particular molecule in each case being responsible to a large extent for considerable variations in their mutual intensity relationships. The significance of such a splitting of the oscillation frequency associated with this linkage is probably intimately connected with the hydrogen atom, a view which finds further support in that the frequency at 1450 which is also characteristic of this linkage is invariably broad and diffuse. It is of interest to note here that the degree of polarisation of the components of this band in any particular substance varies within wide limits, some of them being well polarised and others almost unpolarised.

In this connection the broad bands given by water and ammonia are of considerable interest in that a hydrogen atom is involved in both of them. It must however be remembered that in these two cases there may be a further complication introduced by the polarity of the groups but the evidence available is not conclusive.

The authors desire to express their best thanks to Prof. Sir C. V. Raman for his kind interest in the work.

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[6] See also allyl alcohol, A. S. Ganesan and S. Venkateswaran, Ind. Jour. Phys , Vol. IV, p. 195 (1929).

11

Raman Effect in some Organo-metallic and Heterocyclic Compounds.

BY

S. VENKATESWARAN.

(*Received for publication, 7th June, 1930.*)

ABSTRACT.

The paper describes the results of a study of the Raman spectra of two simple organo-metallic compounds, namely, zinc methyl and zinc ethyl and two typical heterocyclic compounds belonging to the five membered ring group, *viz.*, thiophene and pyrrole. Besides those connected with the presence of the hydrogen atom, zinc methyl gives three distinct frequencies which suggests that the molecule is of the nonlinear type. Following Dennison the dynamics of the system ZnX_2 are worked out and these three frequencies identified with the respective modes of oscillation of the system. Comparison of the spectra of SO_2 and ZnX_2 shows certain similarities, but while the principal line arising from the symmetrical oscillation in the former is remarkably sharp the corresponding one in ZnX_2 is distinctly diffuse towards the violet. It is suggested that this difference in structure in the principal oscillations of the two systems may possibly be due to the presence of isotopes in zinc.

Thiophene and pyrrole show a prominent nebulosity accompanying each incident line which is a rotational effect. The origin of the different frequencies in the two compounds is indicated. A polarisation study of the scattered radiations in thiophene shows that while the classically scattered and the Raman lines are polarised, the nebulosity is practically unpolarised.

1. *Introduction.*

Although the Raman spectra of a number of organic and inorganic compounds have been studied in several laboratories during the last two years, no attention has so far been paid to organo-metallic compounds. Investigations on the Raman spectra of a number of organo-metallic compounds have been undertaken by the author and the results on two of the simplest of them, namely, zinc methyl and zinc ethyl are reported for the first time in this paper. Pyridine [1] and piperidine [2] being the only two heterocyclic compounds studied so far it was thought that it would be of interest to study a few more such compounds. Two typical heterocyclic compounds, *viz.*, thiophene and pyrrole, one containing sulphur in the ring and the other containing nitrogen have been investigated also for the first time and the results are reported here.

All the chemicals used were supplied by Messrs. Scherring Kahlbaum. Zinc methyl was supplied in small phials of 1 cc. capacity and the sample as received showed a prominent continuous spectrum presumably due to some fluorescent impurity. As the substance is spontaneously inflammable in air a special arrangement was made to purify the liquid by distillation. A wide mouthed thick walled Kjeldahl flask was taken and a Wood's tube was fused to its neck through a side tube. After dropping the zinc methyl bulbs carefully into the flask, a constriction was drawn near its mouth which was sealed off after evacuating the apparatus for a sufficiently long time with a hyvac Cenco pump. By shaking the contents in the flask the small bulbs containing the zinc methyl were broken and the liquid was distilled twice over warm water into the Wood's tube. The distilled liquid was free from fluorescent impurities. In the case of zinc ethyl the liquid was obtained in sealed tubes of about 10 cc. capacity and further purification was not considered necessary as the liquid did not show appreciable continuous spectrum. Pyrrol and thiophene were carefully purified by repeated slow distillation in vacuum in a bulb and tube arrangement. Hilger quartz E2 spectrograph was used.

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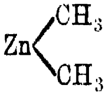
[1] S. Venkateswaran,—J. Phy. Chem., Vol. 34, p. 145, 1930. See also A. S. Ganesan and S. Venkateswaran, Ind. J. Phys., Vol. IV, p. 195, 1929.

[2] G. B. Bonino and L. Brüll,—Gazz. Chim. Ital., Vol. 59, p. 675, 1929.

2. *Results with Zinc Alkyl Compounds.*

In the following tables are given the results of analysis of the Raman lines in the liquids studied. The intensities of the Raman lines (I), their wave numbers (ν) and the shifts in wave numbers ($\Delta\nu$) are given under the respective columns. The incident exciting lines 3650·1, 3654·8, 3663·3, 4046·6, 4077·8; 4339·3, 4347·5 and 4358·3 are represented by the letters *a*, *b*, *c*, *d*, *e*, *f*, *g* and *h* respectively.

TABLE* I, Zinc methyl,



$Zn\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$

I	ν	$\Delta\nu$	I	ν	$\nabla\nu$	I	ν	$\Delta\nu$
0	25208	*d* + 503	1*dc*	24010	*e* − 506	10*dr*	22431	*h* − 507
0*b*	24459	*b* − 2895	5*dc*	23543	*d* − 1162	2*b*	22320	*h* − 618
0*b*	24396	*c* − 2894	2	23437	*h* + 499	8*b*	21822	*d* − 2883
5*dv*	24199	*d* − 506	0	23349	*e* − 1167	8*dr*	21772	*h* − 1166
2*b*	24089	*d* − 616	0	23262	*d* − 1443	0	20050	*h* − 2888

$\Delta\nu$:—506 (10*dv*), 617 (2*b*), 1165 (8*dc*), 1443 (0), 2883 (8*b*).

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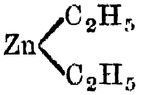
* The following abbreviations are used :—
d :—diffuse, *b* :—broad, *dv* :—diffuse towards the violet, *dr* :—diffuse towards the red.

TABLE II, Zinc ethyl,

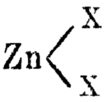


$$Zn\langle^{C_2H_5}_{C_2H_5}$$

I	ν	Δν	I	ν	Δν	I	ν	Δν
0	25182	*d* + 477	0	23369	*d* — 1336	10*b*	21834	*d* — 2874
0	24443	*d* — 262	1	23410	*h* + 472	10*de*	21764	*h* — 1174
10*de*	24231	*d* — 474	0	23342	*e* — 1174	0	21606	*h* — 1332
1*b*	24148	*d* — 557	0	23244	*d* — 1461	0	21529	*g* — 1466
1	24039	*e* — 477	0	22681	*h* — 257	0	21466	*h* — 1472
0*b*	23772	*d* — 933	10*de*	22465	*h* — 473	2*b*	20072	*h* — 2866
0*b*	23718	*d* — 987	1*b*	22380	*h* — 558			
10*de*	23531	*d* — 1174	0*b*	21962	*h* — 976			

Δν :—259 (0), 474 (10*de*), 558 (1*b*), 933 (0*b*), 987 (0*b*), 1174 (10*de*) 1334 (0), 1466 (0), 2874 (10*b*).

The spectrum of zinc methyl is of great interest as it is one of the simplest of organo-metallic compounds. It shows Raman lines corresponding to five frequencies, *viz.*, Δν 506, 617, 1165, 1413, and 2883. Of these the last two are evidently connected with the presence of the hydrogen atom and arise from the C—H linkage. The remaining three frequencies may naturally be attributed to the oscillations arising from the group



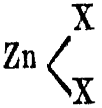
$$Zn\langle^{X}_{X}$$

where X represents the (CH_3) group as a whole. The character of these three lines throws considerable light on the molecular configuration and may therefore be noted. The lines due to Δν 506 and 1165 are very prominent and are definitely diffuse towards the violet. The line at Δν 617 is very diffuse and much less intense than the other two. In zinc ethyl the same character of the spectrum is observed, but owing to the greater complexity of the molecule a number of additional lines appear. The values of the Raman frequencies for the two liquids with their intensities in brackets are tabulated below for comparison.

TABLE III

Zinc methyl		506 (10dv)	617 (2b)			1165 (8dv)		1443 (0)	2883 (8b)
Zinc ethyl	259 (0)	474 (10dv)	558 (1b)	933 (0b)	987 (0b)	1174 (10dv)	1334 (0)	1466 (0)	2874 (10b)

Besides the oscillations arising from the presence of the hydrogen atom, it is seen that $\Delta\nu$ 506, 617 and 1165 of zinc methyl correspond to 474, 558, and 1174 of zinc ethyl. There is a large decrease in the value of the first two shifts in zinc ethyl while the third remains practically unaltered in the two compounds. In both cases the first and the third are very intense and are diffuse towards the violet while the second one is comparatively weak and more diffuse. As already mentioned these three frequencies may definitely be associated with


$Zn\langle^{X}_{X}$ group which is present in the two alkyl compounds.

Zinc ethyl shows two frequencies at 933 and 987 not present in zinc methyl. These are diffuse and weak and arise from the carbon chain present in the former.

Dennison[3] has shown that a correlation of the natural frequencies with the molecular structure of the medium is possible from purely dynamical considerations. Ignoring the coordinates corresponding to the angular and linear momentum of the system as a whole he has shown that the characteristic determinant of a triatomic molecule of the type AX_2 may be written in the form

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[3] D. M. Dennison, Phil. Mag., p. 195, 1926.

$$\left(\frac{m\lambda}{K'}-1-\frac{2m}{M}\sin^2\alpha\right)\left\{\left(\frac{m\lambda}{K'}\right)^2-2\left(\beta+\frac{1}{2}+\frac{m}{M}\cos^2\alpha\right)\frac{m\lambda}{K'}+\frac{2\beta}{\mu}\cos^2\alpha\right\}=0$$

where m and M are the masses of the X and A atoms respectively and K and K′ the forces between X and X and A and X respectively, α is half the angle at the apex of the triangle, $\beta=\frac{K}{K'}$ and $\mu=\frac{M}{2m+M}$. When α has a value other than 90° the system is nonlinear and nondegenerate. Such a system may be expected to give three and only three natural frequencies. The molecule of SO_2 which is known to be nonlinear may be taken as typical of this system and the investigation of the Raman spectrum of this compound by Bhagavantam[4] affords a striking confirmation of the above theory.

Taking the case of zinc methyl we may as a first approximation treat the CH_3 group as a single unit and the molecule may be regarded as belonging to the type AX_2. From a comparison of data of zinc methyl and zinc ethyl it was shown that there are three prominent frequencies which may definitely be associated with ZnX_2 group. The presence of these three frequencies, *viz.*, $\Delta\nu$ 506, 617 and 1165 indicates that the model is of the nonlinear type. The transformations performed in deducing the above determinant for the AX_2 system suggest that of the three modes of oscillation, in the one corresponding to the linear root the zinc atom vibrates in the plane of the triangle along a line perpendicular to the

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S. Bhagavantam, Ind. J. Phys., Vol. V, p. 59, 1930.

symmetry axis, the distance between (CH_3) groups remaining fixed. In the two modes of vibrations corresponding to the other two roots of the equation the zinc atom vibrates along the line of symmetry, the two (CH_3) groups moving apart or moving towards each other symmetrically. From the nature of the factor that gives rise to the linear root it will be seen that the constant associated with the molecular force between the X groups does not affect the frequency of the corresponding oscillation. Hence, it may be expected that a lengthening of the alkyl chain of this configuration should leave this frequency more or less unaffected. Such a view is fully supported from a comparison of the two alkyls studied here. Of the three frequencies associated with the ZnX_2 group the one at $\Delta\nu$ 1165 remains practically unaltered although there is a large difference in the corresponding values of the other two. The Raman lines at $\Delta\nu$ 1165 may therefore be reasonably associated with that mode of oscillation in which the zinc atom vibrates in a line perpendicular to the symmetry axis. Of the other two frequencies the more prominent one at 506 which is also the most intense in the spectrum probably corresponds to the symmetrical oscillation from analogy with the Raman spectra of other compounds where such symmetric oscillations give rise to the most prominent Raman lines. The Raman line shifted by 615 wave numbers which is the only one not yet accounted for evidently corresponds to the third mode of oscillation where the zinc atom goes outward vibrating along the line of symmetry, the two (CH_3) groups moving towards each other. It should be noted here that owing to the presence of three arbitrary constants (a, K, and K') in the equation connecting the kinetic and potential energy functions, beyond stating in a general way that an AX_2 system gives rise to three distinct types of oscillations it is not possible to deduce theoretically a value for the magnitude of any of them.

As both SO_2 and Zn X_2 belong to the nonlinear model it is of interest to compare the Raman spectra of these two compounds. Liquid sulphur dioxide shows three frequencies 526, 1146 and 1340, of which the first and third are weak and diffuse while the lines corresponding to $\Delta\nu$ 1146 which is the principal oscillation is remarkably sharp and intense. Since the atomic forces and the values of a may be expected to differ from each other considerably in SO_2 and ZnX_2 the differences in the magnitude and the relative intensities of the Raman frequencies in the two compounds is not surprising. The two spectra, however, show great resemblance in that both of them give rise to only three Raman frequencies. The principal frequencies $\Delta\nu$ 1146 of sulphur dioxide and 506 of zinc methyl have presumably a similar origin and arise from the symmetrical oscillation of the groups. The low value in zinc methyl is evidently connected with the higher atomic weight of the metal. Such a similarity in origin results as may be expected in a close resemblance between the two corresponding Raman lines. We may cite for instance the degree of polarisation of these lines. According to Bhagavantam[5] the ratio of the weak to the strong component of the principal Raman line in SO_2 is 0·25. The polarisation of zinc ethyl has been studied by the author and it is found that the principal line arising from the symmetrical oscillation of the ZnX_2 group is also polarised to an identical extent, the actual ratio of the two components being 0·25. One would therefore expect that the spectral nature of these two principal lines would be exactly alike. Surprisingly, however, a distinct difference is noticed in the two compounds, namely, that while the line ($\Delta\nu$ 1146), is extraordinarily sharp in sulphur dioxide, the corresponding lines in zinc methyl and zinc ethyl are somewhat broad, definitely tending to be weaker and more diffuse on the violet side. A probable explanation for this anomalous character of the oscillation due to the presence of zinc as contrasted with that of sulphur may be found in the fact that while zinc has several isotopes (ranging in atomic weight from 64 to 70), sulphur has none.

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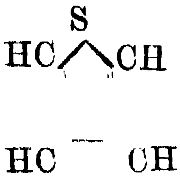
[5] *loc. cit.*

TABLE IV.

C_4H_4S. Thiophene

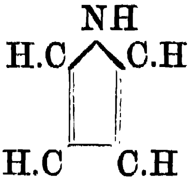


I	ν	Δν	I	ν	Δν	I	ν	Δν
0	24304	a−3085	4	23626	d−1079	5	21902	h−1036
4	24277	a−3112	0	23481	e−1035	4dr	21855	h−1083
1	24243	b−3111	0	23435	e−1081	3b	21621	d−3084
0	24210	c−3080	5	23345	d−1360	6	21592	d−3113
2	24176	c−3114	6	23296	d−1409	4	21575	h−1363
3	24099	d−607	0	22486	h−452	6	21529	h−1409
0b	23954	d−754	4	22331	h−607	0	21391	e−3125
6dr	23870	d−835	1b	22185	h−753	2	19820	h−3118
5	23672	d−1033	6dr	22103	h−835			

Δν :—452(0), 607(4), 752(1b), 835(6dr), 1035(5), 1081(4), 1361(4), 1409(6), 3083(3) 3116(6).

TABLE V.

C_4H_4NH. Pyrrole



I	ν	$\Delta\nu$	I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
6	24253	$a-3136$	1b	23367	$e-1149$	0	21849	$g-1146$
1	24219	$b-3135$	5b	23321	$d-1384$	8	21792	$h-1146$
0	24075	$\left\{\begin{matrix} d-627 \\ a-3314 \end{matrix}\right\}$	3	23235	$d-1470$	0	21733	$h-1205$
			0b	22408	$h-530$	0b	21648	$d-3057$
1	24001	$d-704$	0	22310	$h-628$	6dr	21566	$\left\{\begin{matrix} d-3193 \\ h-1372 \end{matrix}\right\}$
0b	23870	$d-835$	0	22235	$h-703$			
1	23705	$d-1000$	0b	22087	$h-851$	2	21468	$h-1470$
10	23563	$d-1142$	0	21932	$h-1006$	0b	21337	$d-3308$
0b	23506	$d-1199$	0	21890	$f-1149$			

$\Delta\nu$.—530(0), 628(0), 704(1), 843(0b), 1003(1), 1144(8), 1202(0), 1884(4b) 1470(3), 3057(0), 3139 (6), 3308(0b).

In addition to the lines shown in the above table there is a broad band extending from λ4196 to 4165.

3. *Heterocyclic compounds.*

As already mentioned the only two compounds whose Raman spectra have hitherto been studied are pyridine and piperidine. These may be considered as being formed by the substitution of a carbon atom with nitrogen in the benzene or cyclohexane nucleus and belong to the series of compounds having six membered rings. On the other hand thiophene and pyrrole have been chosen for study in this paper since they represent a different class of compounds, namely, those containing five members in the ring. Both show structural resemblance and their spectra are relatively simple. One striking feature of the spectra of these compounds is the large amount of nebulosity or broadening accompanying each of the incident lines. Of the two, thiophene shows it more prominently. This point will be more fully dealt with under the section on polarisation.

Thiophene gives Raman lines corresponding to nine frequencies, all of them more or less equally intense with the exception of 452 and 752 which are comparatively feeble. In pyrrole many of the lines are feeble and in addition a broad weak band extending from λ 4196 to 4165 is observed. Comparing thiophene and pyrrole we find that a Raman frequency at 1374 is prominent in both. This frequency is also prominent in all unsaturated compounds having a double bond between the carbon atoms such as ethylene, allyl alcohol, allyl chloride etc. A theoretical calculation on the basis of the formula $\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}}$ taking Grimm's data for the thermal dissociation constant between $C=C$ gives 1330 for oscillation frequency of this linkage. As both thiophene and pyrrole contain two such $C=C$ linkages we may reasonably attribute the Raman lines at $\Delta\nu$1374 in these compounds as arising from the presence of this linkage in the molecules. The Raman lines at $\Delta\nu$ 607 and 835 in thiophene probably correspond to 655 and 800 in carbon disulphide.

Of the remaining frequencies $\Delta\nu$ 1409, 3083 and 3116 of thiophene and the corresponding ones of pyrrole may definitely be stated to have their origin in the oscillations due to the C—H linkage. It is interesting to compare the stucture of the 3μ band given in these compounds with those obtained in other hydrocarbons. The variations in magnitude and intensity of the components of this band in the various hydrocarbons has already been discussed in detail in the previous paper. Unsaturation is usually accompanied by a high value of these frequencies. It may be pointed out here that in thiophene and pyrrole the CH band assumes a value higher than those of the principal components of this band in the aliphatics or in benzene. This may presumably be connected with the presence of two fixed double bonds in these compounds unlike benzene. The frequency 3116 (3·21μ) of thiophene agrees with the value obtained by Coblentz in the infra-red absorption spectra, *viz.*, 3·22μ.[6]

The ultra-violet absorption spectra of pyrrole and thiophene show a strong periodicity of 1150 cm^{-1} which remains practically unaltered in the entire series of absorption bands.[7] This can evidently be identified with one of the prominent internal oscillation frequencies of the molecules in the excited state. In the Raman spectra this presumably corresponds to $\Delta\nu$ 1384 which is also the prominent frequency common to both the compounds. The difference is due to the fact that the latter has its origin in the unexcited molecules.

We shall now point out certain differences which are noticeable between the spectra of these two compounds. Thiophene gives two prominent lines at $\Delta\nu$ 1035 and 1081 which are absent in pyrrole. The most prominent Raman line in the spectrum of pyrrole corresponds to a shift of 1144 wave numbers which is absent in thiophene. This frequency does not occur in methyl, ethyl or triethylamines, but occurs with some prominence in aniline and dimethylaniline. The exact nature of its origin is not at present clearly understood.

Pyrrole shows a broad Raman line shifted by 3311 wave numbers which is not present in thiophene. Such a frequency occurs in ammonia and all the alkyl and aromatic primary and secondary amines and is evidently due to the presence of the NH group. There is also a weak line at 1003 in pyrrole which is not present in thiophene. This frequency appears in all the amino compounds and may be associated with the C—N *linkage.*

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[6] Coblentz, Inv. of Infra-red Spectra, p. 98 (1905).

[7] S. Menczel :—Zeits. f. Phys. Chem. 125, 161, 1927.

4. *Polarisation of the Raman lines in thiophene.*

The polarisation has been spectroscopically investigated by placing a nicol in the path of the scattered light. A two prism glass spectrograph was used for the purpose which on calibration was found to introduce a 40 per cent polarisation in the initially unpolarised light. Hence the necessary corrections were introduced in the exposures. An examination of the spectrograms shows that the different mercury lines corresponding to the classical scattering are polarised more or less to the same extent. On the other hand, the Raman lines are all polarised to different extents. The following table gives the depolarisation values of the Raman lines corresponding to the different frequency shifts.

TABLE VI

$\Delta\nu$	607	752	835	1035	1081	1361	1409	3083	3116
γ	0·25	0·80	0·20	0·17	0·50	0·25	0·40	0·75	0·25
I	4	1	5	5	4	4	5	3	5

γ = ratio of the weaker to the stronger component.
I = Intensity of the Raman line.

From the above table it is seen that all the well polarised Raman lines are also the more intense. It is interesting to note that the components of the 3μ band due to the CH linkage are differently polarised, the one at 3083 being much less polarised than the one at 3116. Such differences in the degree of polarisation of the components of the 3μ band arising from the CH linkage are also noticeable in the case of the aliphatic compounds.

Unlike the above two cases of the classically scattered and the Raman lines, the nebulosity accompanying each incident line is almost unpolarised. In the first instance it may be noted here that the nebulosity extends symmetrically on either side of the incident lines. This suggests that it is a rotational effect. In this respect thiophene presents a case closely analogous to benzene or carbon disulphide. A ring compound may be expected to possess a high degree of optical asymmetry which in this case is evidently further intensified by the presence of the sulphur atom. In accordance with the view expressed by Raman and Krishnan[8] such a prominent rotational effect in thiophene may be connected with the high anisotropy of the molecule. Its relatively low polarisation as contrasted with some of the Raman lines associated with pure vibration is also in agreement with what we should expect theoretically according to Hill and Kemble.[9]

The author desires to express his best thanks to Prof. Sir C. V. Raman, F.R.S. for his kind interest in the work.

210, Bowbazar Street,
Calcutta.

[8] C. V. Raman rnd K. S. Krishnan. Nature 122, p. 852, Dec. 8, 1928.

[9] E. L. Hill and E. C. Kemble, Proc. Nat. Acad. Vol .15, p. 387, 1929.

12

On the Intensities of the Lines in Raman Spectra.

By

S. C. Sirkar, M.Sc.

(Received for publication, 1st July, 1930.)

Abstract.

The relative intensities of the Raman lines due to CCl_4 excited by the mercury lines 4358 A, 4046 A and 3132 A, as well as those of the undisplaced scattered lines of the said wavelengths have been measured by the method developed by Merton and Nicholson. It has been found that the intensities of the Raman lines excited by the mercury lines 4046 A and 3132 A relatively to those excited by the line 4358 A are respectively 1·17 times and 1·38 times more than is indicated by the Rayleigh fourth power law. It has been also shown that the results obtained very recently by Orustein and Rekveld also indicate a deviation from the fourth power law in the case of the displaced lines excited by the line 4046 A.

The ratio of the intensity of the third shifted CCl_4 line to that of the exciting undisplaced radiation 4358 A has been found to be about 1/410 and for all the shifted lines taken together, this ratio is found to be about 1/150.

1. *Introduction.*

Soon after the discovery of the Raman effect, Raman and Krishnan[1] made observations with liquid carbon tetrachloride, which seemed to indicate that the intensity of the modified lines increases with the reciprocal of the wave-length of the exciting radiation more rapidly than is indicated by

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[1] C. V. Raman and K. S. Krishnan. Proc. Roy, Soc. 122, p. 23, 1929.

Rayleigh's inverse fourth power law. A few months later, Daure[1] made some quantitative measurement of the ratio of the intensities of the undisplaced lines 5460 A and 4358 A scattered by the liquid $AsCl_3$ and also that of the Raman lines of same frequency excited by these lines. His measurements indicated that the intensity of the Raman lines does not increase with frequency so rapidly as is indicated by the fourth power law. He repeated his measurements subsequently and showed[2] that in the case of $AsCl_3$ and CCl_4, the ratio of intensity of the displaced lines of the same frequency, excited by the lines 4358 A and 5460 A of mercury, is equal to that of the exciting lines of the said wave lengths in the scattered spectrum. Recently Ornstein and Rekveld[3] have compared the intensities of the mercury lines 5460 A, 4358 A and 4046 A as given out by the Heraeus quartz mercury lamp and also that of the displaced lines of the same frequency in the spectrum scattered by CCl_4. According to these observers, the displaced lines in the visible region of the spectrum obey the Rayleigh fourth power law very accurately. The object of the present paper is to investigate the question more fully and especially to consider the ultra-violet region of the spectrum.

2. *Preparation and Calibration of Photometric Wedge.*

The method developed by Merton and Nicholson[4] has been used in the present investigation for comparing intensities of different lines. As glass wedges are unsuitable for investigation in the ultra-violet region, a platinum wedge obtained by sputtering platinum on quartz plate, was used. It has been shown by Merton[5] that such a platinum wedge is suitable for investigation in the ultra-violet region. It was observed, while making the wedge by sputtering, that a gradient in the thickness of the deposit could be very easily obtained by using a flat horizontal platinum cathode and keeping the quartz plate just below it with any other smaller plate placed in an inclined position on the quartz plate so as to obstruct partly the direct beam of sputtered particles. It was found that there was a gradient in the thickness of the platinum deposited on the larger quartz plate in the directions at right angles to the edges of the screening plate. The deposit was protected by placing another quartz plate on it and joining the two plates together, with paper pasted at the edges. A very small portion was chosen where the gradient in thickness seemed to be uniform and the whole plate was covered up with black paper leaving a small slit of length about 6·5 mm. at the portion chosen. As there was no neutral glass wedge available, the platinum wedge was calibrated in the following way. The wedge was placed almost in contact with the slit of the spectrograph with the direction of gradient parallel to the length of the slit and the image of a Heraeus mercury lamp, placed vertically, was focussed on the slit with two small quartz lenses of aperture having diameter about 2·5 cm. placed so that the lamp and the slit were placed almost at the focal points of the two lenses respectively. Metal plates, in one of which there was a circular aperture about 2 cm. in diameter, and the others having different number of holes, about 1·78 mm. in diameter, drilled within the same area as that of the aperture, were placed one by one between the lenses, and photographs were taken on the same plate with the same exposure for each metal plate. Ilford Rapid Process Panchromatic plates were used and a dilute cutting solution of potassium ferricyanide was used to remove the chemical fog. The " density " of two successive metal plates corresponded to the difference of the lengths of the same line on the two successive photographs corresponding to the two metal plates. The lengths of the lines were measured under an Adam Hilger travelling microscope. The magnification at different parts of the spectrum was also determined and all the measured lengths were corrected for magnification. The results obtained from the calibration plates are given in Table 1. Several plates were taken and those results which were obtained consistently in all such plates are collected in the table. Results with metal plates having smaller number of holes were found to be unreliable and have been rejected.

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[1] P. Daure, Comptes Rendus, 187, p. 826, 1928.

[2] P. Daure, Comptes Rendus, 188, p, 1605, 1929.

[3] Ornstein and Rekveld, Zeit. f. Phys. 61, p. 593, 1930.

[4] Merton and Nicholson, Phil. Trans. A, Vol. 217, p. 237, 1917.

[5] T. R. Merton, Proc. Roy. Soc. 106, 378, 1924.

TABLE 1.

Wavelength in A.U.	Initial length from the thin end in mm.	Final length from the thin end in mm.	Difference in mm.	Total density.	Density per mm.
4916	5·076	3·290	1·786	0·436	0·244
4046	5·31	3·797	1·513	0·436	0·288
,,	4·826	3·471	1·355	0·436	0·322
,,	3·471	2·775	0·696	0·265	0·380
,,	2·775	2·103	0·672	0·143	0·213
3751	4·420	2·504	1·916	0·701	0·365
3342	4·867	3·684	1·183	0·418	0·352
,,	4·478	3·197	1·281	0·436	0·341
,,	3·684	2·901	0·783	0·283	0·362
,,	3·197	2·512	0·685	0·265	0·386
,,	2·901	2·339	0·562	0·143	0·254
,,	2·512	1·925	0·587	0·143	0·243
2910	4·101	2·995	1·106	0·436	0·394
,,	2·995	2·180	0·815	0·265	0·325
,,	2·180	1·610	0·570	0·143	0·250
2804	5·370	3·718	1·652	0·701	0·423
..	1·718	0·800	0·918	0·265	0·288

It will be noticed that the density per mm. of the length of the wedge at different parts of its length is not constant, and also that the whole wedge has different densities for different wavelengths. It is however possible to calculate the density of any length of the wedge, measured from the thin end, by interpolation, assuming that there is no discontinuity within 1 mm. from the thin end. No such discontinuity could be visually observed and the results for the wave length 2804 indicate to some extent an absence of such a discontinuity. It is thus possible to calculate the photographic intensity of any line, which is equal to $\log^{-1}_{10}$ (density of a length of the wedge from its thin end equal to the length of the line).

3. *Test of the Rayleigh Fourth Power Law.*

Kahlbaum's carbon tetrachloride was distilled in vacuum several times and a quartz tube, about 20 cm. long and 2·5 cm. in diameter was washed several times with the distilled liquid and finally filled up with it. The quartz tube was closed at both ends, one of the ends being quite flat and transparent and the other being rounded and painted black outside. It was also provided with a small side tube to introduce the liquid and it was closed with a glass stopper. In obtaining the scattered spectrum, extraneous light was cut off in the following way. The Heraeus mercury lamp was placed horizontally parallel to the quartz tube, both the tube and the lamp lying in a horizontal plane. A real image of about unit magnification, of the flat end of the quartz tube was formed by a quartz lens on the slit of the spectrograph. A tube of black paper was placed between the lens and the flat end of the quartz tube to prevent external light from falling on the lens and another such tube was placed between the lens and the slit. The other end of the quartz tube being blackened outside, provided a black background. The image of the flat end of the quartz tube formed by the quartz lens on the slit consisted of a faint bluish circular patch surrounded by a white and comparatively bright rng due to the light diffused by the walls of the quartz tube. The central blue patch was formed by light scattered by the liquid and as it was about 2 cm. in diameter while the length of the slit used was only 6·15 mm, it was possible to have the whole length of the slit uniformly illuminated by the scattered light. After a few preliminary photographs of the scattered spectrum were taken, it was found that the liquid was absorbing the ultra-violet lines and this absorption increased so much when the liquid was exposed to ultraviolet rays for a long time, that the line 3132 was almost completely absorbed. It was, however, found that on cutting off the extreme ultra-violet lines beyond 2890 by placing a clean sheet of mica between the lamp and the quartz tube, there was no such change in absorption.

An attempt was made to find out how far the undisplaced stattered lines obeyed the Rayleigh fourth power law with the foregoing arrangement. In doing so, the photograph of the incident spectrum also was taken through the mica filter. The results obtained showed that the fourth power law was obeyed relative to the 5460 A line in the visible region up to the line 4358 A, beyond which there was still some absorption in the ultra-violet region. A rough estimation of the coefficient of absorption was made in the following way. Photographs of scattered spectrum were taken on the same plate with different lengths of the quartz tube, measured from the flat end, exposed to the mercury lamp. It was found on measurring the lengths of the lines, that the ratio of the intensity of either of the lines 4046 A and 3132 A to that of 4358 A was slightly greater for shorter lengths of the liquid column, than for longer lengths. Let Io denote the intensity of light scattered along the length of the tube per unit length of the liquid column and let β be the coefficient of absorption. When the whole length l of a liquid column is illuminated by the mercury lamp placed parallel to it, the intensity of the scattered light emerging from the flat end is given by

$$I = I_o\int_0^l e^{-\beta x}\,dx = \frac{I_o}{\beta}\left(1-e^{-\beta l}\right)\ldots\ldots\ldots\ldots(1)$$

Let a_1 and a_2 be the ratios of intensity of a particular wave length which is absorbed to that of a wave length which is not absorbed, for lengths l_1 and l_2 of the liquid column exposed to the mercury lamp. It follows from equation (1) that

$$\frac{1-e^{-\beta l_1}}{1-e^{-\beta l_2}} = \frac{a_1\, l_1}{a_2\, l_2}$$

$$\text{or} \quad a_2\, l_2 - a_1\, l_1 = a_2\, l_2\left(1-e^{-\beta l_1}\right) - a_1\, l_1\left(1-e^{-\beta l_2}\right) \quad \ldots\ldots\ldots\ldots(2)$$

Equation (2) can be solved graphically and the value of β can thus be found out. Table II shows the results obtained.

TABLE II.

Wave length in A. U.	Intensity compared to that of 4358A line.	Length of liquid column exposed.	$\frac{l_1}{l_2}$	β	Mean value of β
4046	·07	2·5 cm.			
,,	·89	6·5 ,,	$\frac{2·5}{6·5}$	0·044	0·0455
,,	·84	8·9 ,,	$\frac{2·5}{8·9}$	0·047	
3132	·436	2·5 ,,			
,,	·390	6·5 ,,	$\frac{2·5}{6·5}$	0·060	0·066
,,	·350	8·9 ,,	$\frac{2·5}{8·9}$	0·072	

In obtaining photographs of the scattered spectrum for verification of the fourth power law in the case of undisplaced lines, the length of the liquid column exposed was about 13·7 cm. and the results given in Table III were obtained.

TABLE III.

Incident spectrum.			Scattered spectrum.			
λ_1 in A. U.	λ_2 in A. U.	$\frac{I_{(\lambda_2)}}{I_{(\lambda_1)}}$	Observed $\frac{I_{(\lambda_2)}}{I_{(\lambda_1)}}$	Correction factor for absorption	Correctep $\frac{I_{(\lambda_2)}}{I_{(\lambda_1)}}$	$\frac{I_{(\lambda_2)}}{I_{(\lambda_1)}}$ Calc. from 4th power law.
5460	4358	6·21	15·28	1·0	15·28	15·30
5460	4046	5·21	13·44	1·35	18·10	17·30
4358	3132	0·1205	0·3081	1·50	0·462	0·452

4. *Results with Raman Lines.*

Ilford Panchromatic H&D 700 backed plates were used in the foregoing experiments, because these plates had to be used also to obtain the Raman lines with reasonable exposure. An exposure of about 12 hours was necessary to obtain the Raman lines on the plates mentioned above. The undisplaced scattered lines were also photographed on the same plate, with suitable exposure varying from 3 to 6 minutes, before and after the liquid was exposed for obtaining the Raman lines. The relative intensities of the undisplaced scattered lines were found to be the same before and after the long exposure. The relative intensities of the four Raman lines of frequency shifts 216, 313, 459 and 719 excited by the lines 4358 Å and 3132 A were measured while in the case of the line 4046 the intensity of the 3rd shifted line was measured. The mercury lamp was allowed to run for half and hour before any exposure was started. The results given in Table IV. were obtained.

TABLE IV.

Exciting wave-length in A. U.	Photographic intensity of undisplaced line in arbitrary unit.	Wave number difference for Raman lines.	Photographic intensity of Raman lines in arbitrary units.
4358	40·7	216	7·00
		313	7·91
		459	8·63
		791	5·48
4046	35·8	459	8·90
3132	12·6	216	2·85
		313	3·34
		459	3·69
		791	2·30

5. *Discussion.*

It can be concluded from the above results on assuming that the undisplaced lines obey the Rayleigh fourth power law, that the Raman line excited by the 4046 A line is 1·17 times more intense and all those excited by the line 3132 A are about 1·38 times more intense than is indicated by the Rayleigh fourth power law, relative to the 4358 A line. The assumption is justified by the fact that with the same arrangemets, the Rayleigh fourth power law has been experimentally verified, the absorption being taken into account in the ultra-violet region. The existence of absorption in the case of 4046 A line was verified by taking photograph through a Hilger Nutting photometer, a long column of the liquid about 40 cm. in length being used.

It may be mentioned here that throughout the experiment a moderately wide slit of the spectrograph was used. It is well-known that the central intensity of any spectral line, having an appreciable width, is increased as the width of the slit is increased up to certain limit depending on the width of the spectral line. Any further widening of the slit beyond this limit only makes the image of the line broader, without increasing its central intensity. As the central intensity is proportional to the area of the λ-intensity curve intercepted by the λ axis, it is also proportional to the integrated intensity, *i.e.*, the total energy in that line. The total energies in different lines can thus be compared by measuring the central intensities, a moderately wide slit of the spectrograph being used.

The ratio of the intensity of each of the four Raman lines to that of the exciting undisplaced scattered line was determined for the exciting line 4358 A. It was found that for the third and the strongest Raman line, the ratio is about $\frac{1}{410}$ and for all the four modified lines taken together, the ratio is about $\frac{1}{150}$.

The results obtained indicate that in the case of Raman scattering, there is deviation from the Rayleigh fourth power law, which increases as the incident frequency approaches the ultra-violet absorption line of the liquid. Liquids having absorption lines nearer to the visible region than in the case of CCl_4 may therefore show a deviation in the visible region also. Further investigations on this point are in progress. It may be mentioned here that the results obtained by the author are not inconsistent with those obtained by Ornstein and Rekveld[1], because the latter have overlooked the slight absorbing power which the liquid possesses in the region of 4046 A and have still found that the Raman lines excited by this line exactly obey the fourth power law, and if this absorption is taken into account, it is evident that their results will indicate a deviation from the fourth power law.

The author's grateful thanks are due to Sir C. V. Raman F.R.S., who kindly suggested the problem and under whose kind guidance the work was carried out.

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[1] Ornstein and Rekveld, *loc. cit.*

13

Relation of Raman Effect to Crystal Structure and Properties of Diamond.

By

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(Received for publication, 3rd July, 1930.)

(Plate IX.)

Abstract.

The results of a study of the Raman effect and certain attendant phenomena in nine different samples of diamond are described. All of them show Raman lines corresponding to one well defined frequency shift 1331·9 ± 0·3, the value of which does not show any detectable variation from diamond to diamond. In perfect and colourless samples, the Raman lines are usually very intense and sharp, whereas in blue diamonds there appears to be a weakening of the absolute intensity. In one rather poor sample the line presents a distorted appearance. There is present in all cases, except one very yellow sample, a system of three bands at 4131, 4157 and 4174 A.U., the central one being very prominent and extending over 10 A.U. A prominent continuous spectrum often accompanies the above having a well defined limit on the violet side at about 4240 A.U. and extending well into the red end. The intensity of these bands and the continuous spectrum varies in a remarkable way with the specimen studied; they are weak in white diamonds and are particularly conspicuous in blue diamonds for the colour of which they appear to be responsible.

Considering each carbon atom as bound tetrahedrally to its four nearest neighbours and together with them capable of oscillation with respect to the rest of the crystal lattice, a theoretical computation indicates four fundamental oscillations whose wave-numbers are 440, 780, 1306 and 1750. The third gives approximately the frequency-shift of the observed Raman lines and represents an oscillation of the central carbon atom within the tetrahedron. The higher frequencies observed by Robertson and Fox in the infra-red absorption are explained as combinations of the above. Existing data on the specific heat of diamond and other physical properties are briefly discussed in relation to the above frequencies.

1. *Introduction.*

In a recent paper[1] the author gave some measurements of the frequency shifts observed in the Raman effect with diamond. Certain attendant phenomena which were observed suggested that a more detailed study with as many different samples of diamond as possible would be of interest. The present paper describes the experimental results obtained with nine diamonds of different colours, sizes and degrees of perfection. The relation between the observed phenomena and the crystal structure and other properties of diamond are discussed in detail.

2. *Experimental results.*

The light of a quartz mercury arc is focussed by means of a glass condenser on to the diamond which is so mounted that the reflected light is sent in a direction opposite to that of the spectrograph. A two prism glass instrument of high light gathering power supplied by Adam Hilger is used for photographing the spectra of the scattered light.

In the first instance it must be mentioned that with all the diamonds, Raman lines were observed corresponding to one well defined frequency shift of about 1332 wave-numbers, whose value does not show any detectable variation from diamond to diamond. Using Hartman's simplified formula with the mercury lines as standard the following frequency shifts are obtained in a variety of them; five different samples of colourless diamond: 1331, 1332, 1332, 1331 and 1331; yellow diamond: 1330; blue diamond: 1333, 1331. It will be seen that the variations are within the limit of the accuracy of the method. In most cases the transition is excited by the two principal mercury lines 4046 and 4358 A.U., the line arising from the latter being usually the stronger. Three plates have also been measured interpolating linearly between close iron arc lines. The frequency shifts obtained are 1331·7, 1331·9, and 1332·1. Thus the best representative value for the infra-red wave-number may be given as 1331·9±0·3.

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[1] Ind. Jour. Phys., Vol. V, p. 35 (1930). See also Ramaswamy, Nature, Vol. 125, p. 704 (1930) and Ind. Jour. Phys., Vol. V, p. 96 (1930). The effect was described by him first in these communications.

An important feature associated with this line is the extreme sharpness in most cases. Hence the corresponding wave-number may be regarded as a physical constant characteristic of diamond capable of being measured with a high degree of precision. Such an extreme sharpness, according to the views expressed by Sir C. V. Raman, may be connected with the perfection of crystal structure in diamond. In one case however, when the diamond was of a rather poor quality it was found that the sharpness of the line is considerably diminished, the line presenting a slightly distorted appearance. There is also present a feeble companion line on its longer wave-length side and but so diffuse that its genuineness is uncertain.

It is found that under suitable conditions of illumination, this principal Raman line could be photographed with ease in about 5 to 10 minutes in the case of diamonds of moderate size whereas an hour's exposure is usually quite sufficient in the case of even the smallest of those examined. Contrary to this there is however present a certain amount of difficulty in obtaining this line with diamonds of a light blue colour, although it must be mentioned here that there is a much stronger continuous spectrum in the latter case. It will no doubt have to be remembered that the intensity of the scattering depends to a large extent on the particular cut, adjustment and various other factors associated with the examination of each sample. On a close examination of the various plates taken with colourless and with blue diamonds, the author is definitely led to conclude that the greater prominence of the continuous spectrum with the latter cannot alone account for the difficulty of obtaining the Raman lines. It appears that there is a real weakening of the intensity of the Raman lines, along with the development of the continuous spectrum in blue diamonds. See Figs (c) and (f) in Plate IX.

Bands and the continuous spectrum.—Besides the Raman lines there is present a system of three bands at wave-lengths 4131, 4157 and 4174 A.U. The central one is the most intense one and is comprised between well defined limits extending over 10 A.U. *viz.*, from 4152 to 4162. The other two bands are relatively much feebler. It must be mentioned here that on the longer wave-length of the mercury line 4358, there is nothing corresponding to any one of these bands. This result clearly shows that the band does not represent a Raman transition. If it was excited in the manner of a Raman line by the 4046 radiation, it is but natural to expect the 4358 to produce it quite as prominently if not stronger. The light scattered by one of the samples was also photographed with a quartz spectrograph. The spectrum shows the Raman lines excited by the group of lines at 3650 A.U. quite prominently whereas there is nothing excited by this group corresponding to the above bands of the blue violet region. The plate is also free from continuous spectrum in this region. Walter[1] has actually observed bands at 4155 in the absorption spectrum of some diamonds. The effect was marked in some yellow ones, but feeble in red, green and brown diamonds. The fact that there does exist such an absorption frequency

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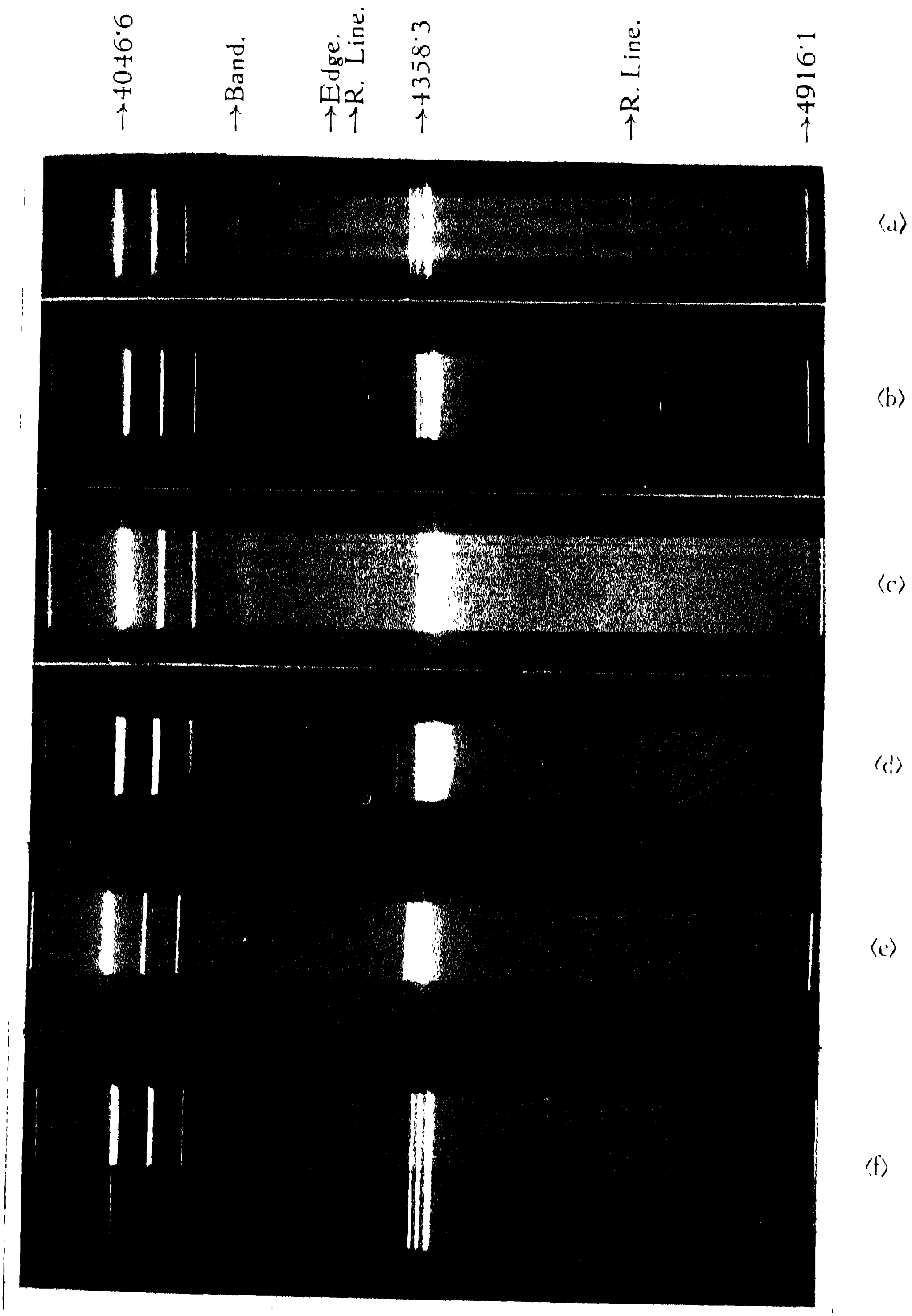
[1] Wied. Ann., Vol. 42, p. 505 (1891).



Raman Spectra of Diamonds.

(a) Light Yellow ; (b) Colourless ; (c) Blue ; (d) Imperfect , (e) Yellow ; (f) Blue ;

in diamonds suggests that they are in the nature of fluorescent radiation.

The intensity of these bands varies in a remarkable manner with the colour of the diamond, (Plate IX). Those having a pale blue colour show the phenomenon most conspicuously (Fig. c), whereas they are much less prominent in colourless diamonds (Fig. b). (Fig. e) was obtained with a diamond of a strikingly yellow colour. It gave feeble Raman lines and a continuous spectrum (without bands) stretching practically over the whole region from 3800 A.U. to the red end. Crookes[1] has recorded various sharp lines in the green and the greenish blue region of the phosphorescent spectrum of diamond excited by exposure to cathode rays. In his work, there is no mention of any bands analogous to those mentioned in this paper. This result is surprising as one would expect them to be excited quite as prominently.

Another striking feature characterising the scattered spectra is the presence of a strong continuous spectrum which appears with a fairly well defined edge on the violet side at about 4240 A.U. and extending well into the red end of the visible spectrum. All the plates taken with various diamonds show a gap between the mercury lines 4916 and 5460. A visual examination through the spectroscope reveals that the continuous spectrum is quite as prominent in this region as in others. The above result is therefore due to the fact that the photographic plate is insensitive in this region. In some cases there is also present a feeble continuous spectrum in the region 3800 to 4100 A.U. The introduction of a filter cutting out the mercury line at 4046 eliminates the bands and practically the whole of the continuous spectrum (Fig. f). Figs. a, b, c and e serve to show very clearly the variation of the above phenomenon in diamonds. Fig. a is a spectrum taken with a diamond having the palest yellow tinge and shows both the Raman lines and the bands accompanied by a continuous spectrum of considerable intensity.

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[1] Phil. Trans., Vol. 170, pp. 135 and 641 (1879). See also Vol. 174, p. 891 (1883).

The continuous spectrum in blue diamonds is so conspicuous (Fig. c) that the aggregate intensity of the same must be very considerable and is probably responsible for its blue colour. One of the samples examined which was ordinarily (in dull light) was of a light blue colour showed a remarkable strengthening of the blue when taken into the bright day light. This sample was illuminated with the near ultra-violet light from a mercury arc lamp by interposing a Wood's ultra-violet filter and was found to emit a marked blue radiation. Becquerel[1] observed in the phosphorescent spectrum of diamond two bands from 4300 to 4860 and 5270 to 6560 A.U. which are probably closely related to the above phenomena.

3. *Relation to Crystal Structure.*

The structure of the diamond lattice has been very thoroughly determined by Bragg and others and is now regarded as a continuous chain of carbon atoms linked to each other in such a manner that every carbon atom is joined to four others tetrahedrally. The lattice is made up of two interpenetrating face-centred cubic lattices. It is reasonable to assume that the observed Raman transition represents an oscillation of individual carbon atoms within the core constituted by the rest of the lattice surrounding each one of them. Such a view is strongly supported from the consideration of the following cases. The author has recently investigated the Raman spectra of various tetra-chlorides having tetrahedral structures.[2] All of them show four frequencies, the third of which is the most prominent. In the series, as we procéed from carbon the lightest to tin the heaviest, this intense line appears to gain in prominence at the expense of others. The cases of SO_4 and ClO_4 have again analogous tetrahedral structures and likewise show one prominent line accompanied by a few other feeble lines.[1] From a consideration of the mechanical vibrations of such a system, the author has identified this line with an oscillation in which the central atom moves about its equilibrium position within the surrounding tetrahedron.[2] All the above cases result in an intense and well polarised Raman line, very much like that of diamond.[3]

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[1] Ann. Chim. Phys., Vol. 55, p. 89 (1759).

[2] *Loc. cit.*

It must however be remembered that in the case of diamond we are not justified in isolating portions of the lattice in as much as it is one big molecule extending to the very boundaries of the crystal. It is but natural to assume that the character of the line will be influenced to some extent by the dimension of the outer core surrounding the oscillating atom. In this connection the theory of mosaic structure developed by Smekal, Zwicky and others is of interest in that it postulates an intrinsic imperfection of crystals. A typical instance of such a mosaic structure showing itself in diamond is actually known and may be cited here. The reflection of Rh—Kα doublet comes out with extreme sharpness from an ideal diamond whereas it shows a large distortion and breadth in an imperfect one.[4] Similar variations in the sharpness of the Raman lines have actually been observed and reported in the previous pages. Such phenomena are evidently connected with the degree of imperfection or mosaic state. Whether the intensity of the Raman line, particularly in blue diamonds, is also influenced by such imperfections is more than can be said just now. To ascertain the precise relation between the mosaic state and the Raman scattering, it is however necessary to examine the same diamond more critically by various methods.

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[1] A. M. Taylor, Mol. Spectra and Mol. Structure, Trans. Far. Soc., p. 830 (1929).

[2] Ind. Jour. Phys., Vol. 5, p. 73 (1930).

[3] Ramaswamy (*loc. cit.*) finds that the line in diamond is well polarised.

[4] Handbuch, Der Ang. Phys. Chem., Band 14, p. 426 (1926).

4. *Relation to Infra-red Absorption.*

Each atom of the diamond lattice may be considered as being influenced by only the four nearest neighbours arranged tetrahedrally, the latter in their turn being bound similarly to others which may be regarded as being rigidly fixed. The mechanical vibrations of such a configuration can be worked out in a manner very similar to that of the AX_4 type. The potential energy function in this case undergoes a slight change in view of the fact that the X atoms are also bound tetrahedrally. If the constant[1] which represents the force between neighbouring carbon atoms in the diamond lattice is taken as $43 \cdot 35 \times 10^4$, it can be shown that the frequencies with which the system is capable of oscillating are given by 440, 780, 1306 and 1750. The analysis shows that 780 and 1750 correspond to a symmetric motion of the outer carbon atoms, whereas 1306 is analogous to the intense oscillation in the tetrahedral models. It can at once be identified with the actually observed one at 1332 and represents an isotropic vibration of the carbon atom within the surrounding core. It is also obvious, by analogy with other cases, that the rest of the postulated frequencies, *viz.*, 440, 780 and 1750 will manifest themselves very weakly in the Raman spectra, if they do so at all. On the other hand, it is quite possible that when the entire lattice is taken into consideration, these frequencies may undergo considerable alterations and thus are more or less virtual.

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[1] The justification for such a value of the constant is that it gives 990 for the C—C oscillation frequency of ethane in perfect agreement with the experimental value.

The case of methane investigated by Dennison[1] is instructive in this connection. Its Raman spectrum[2] has so far revealed only one prominent multiple band at about 3·5μ which is analogous to the principal line in all the above cases and is identified by Dennison with such an oscillation. The other three frequencies demanded by the theory have not however so far been detected at all.

Of the above four calculated frequencies, the one at 1306 corresponds to an optically active oscillation and is represented by one edge of a broad band at 8·02 μ in the infra-red absorption.[3] Why such a sharp line in the Raman spectra should have in the infra-red absorption, a broad band with its centre displaced to one side as its analogue is not clear. This result is of great significance in that it affords a definite case where the infra-red absorption is of quite a different character from that of the Raman line. Of the other three oscillations, those having values 780 and 1750 are optically inactive and accordingly have not been observed by Robertson and Fox in the absorption spectrum.[4] The one at 140 is beyond the region of their investigation.

On the other hand they have detected three more bands at 2086, 2438 and 3353, the last of which has been interpreted by them as having a combinational origin. The former two are regarded as fundamental oscillations characteristic of the diamond lattice. The author is however of the opinion that they all have a combinational origin as the former two may also be represented satisfactorily as summationals of the frequencies postulated above. The table below shows their mutual relationship.

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[1] Astrophys. Jour., Vol. 62, p. 84 (1925).

[2] J. C. Mclennan, H. D. Smith and J. O. Wilhelm, Trans. Roy Soc. Canada, Vol. 23, p. 279 (1929).

[3] Robertson and Fox, Nature, Vol. 125, p. 704 (1930).

[4] Analogous oscillations in methane at 1520 and 4200 appear very feebly in the infra-red absorption. D. M. Dennison, *loc. cit.*

Fundamentals	Raman effect	Infra-red R. and F.	Interpretation
ν_1 : 440	...	...	...
ν_2 : 780	...	Inactive	...
ν_3 : 1306	1332	1246	ν_3
ν_4 : 1750	...	Inactive	...
...	...	2086	2086 : $\nu_2+\nu_3$
...	...	2438	2526 : $\nu_1+\nu_2+\nu_3$
...	...	3353	3392 : $\nu_2+2\nu_3$

The agreement is good in view of the fact that the method is only approximate. It must be mentioned that the above theory is only tentatively put forward.

5. *Relation to Specific Heat.*

The case of diamond is of great interest as it is the classical example of a solid element which does not conform to the Dulong and Petit law of atomic heats. The measurements of Nernst[1] show that the specific heat falls to almost nothing at low temperatures and is not even a thousandth part of what is to be expected on the basis of the above law. The theory developed by Debye for the specific heat of solids enables us to connect the natural frequencies of a lattice with the observed specific heat and its variations with temperature. Θ, the characteristic temperature of the substance is connected with ν_m the maximum oscillation frequency of the lattice by the equation $\Theta=\frac{h\nu_m}{k}$ where h is the Planck's quantum of action and K the molecular gas constant. From the specific heat measurements at moderately high temperatures, the value of this constant is given by Nernst and Lindemann[2] as 1860 which corresponds to a wave-number of about 1300. This is in fair agreement with the observed principal frequency.

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[1] Ann. Der. Phys., Vol. 36, p. 395 (1911).

[2] See Handbuch Der. Physik, Vol. 10, p. 42.

On the other hand such a low value of the characteristic temperature is not in agreement with the observations at low temperatures. The failure of the theory is evidently due to the fact that it assumes a maximum limit for the possible frequencies. The characteristic temperature assumed above, *viz.*, 1860 does not really correspond to the highest of the frequencies for diamond, *viz.*, 1750 according to the calculations given in the previous pages. Simon[1] discussed more fully the available data and was led to explain the observed specific heat variations of diamond as due to a resultant effect of two different functions only one of which is of the Debye type. It is interesting to note here that the characteristic temperature appearing in it, *viz.*, 2340 closely corresponds to the highest of the calculated frequencies, *viz.*, 1750. It may be hoped that a careful consideration of the various theories and further experimentation will lead to a satisfactory explanation of the interesting observations connected with the specific heat of diamond.

6. *Relation to other Physical Properties.*

It is well known that the Debye function of a substance can also be deduced from a knowledge of the Poisson's ratio and compressibility. The results obtained in various cases are in good agreement with the values deduced from specific heat data.[2] In the case of diamond the data for the Poisson's ratio are however not available. On the other hand Grüniesen[3] has given a theory connecting this function with the co-efficient of volume expansion. In the case of diamond it has been worked out by him as 1860 almost in perfect agreement with the value of Nernst and Lindemann at higher temperatures. This again suggests a frequency of 1300 for the lattice.

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[1] Sitz-der Preuss. Akad. der Wiss., Vol. 33, p. 477 (1926).

[2] See Born. 'Dynamik der Kristalgitter.'

[3] Handbuch der phys., Vol. 10, (*loc. cit.*)

Apart from its relation to the above physical constants, it may be expected that such a high frequency of the nuclear oscillations also involves a correspondingly high electronic frequency lying in the far ultra-violet responsible for its large optical refractivity and dispersion. An actual computation on the basis of Haber's square-root formula[1] yields an absorption wave-length of about 500 A. U. for diamond. Such an absorption is too far in the ultra-violet and will not account satisfactorily for the observed refractivity and dispersion of diamond. It will however have to be remembered that Haber's rule involves various assumptions. The significance of the same has been discussed very thoroughly by Born.[2] The rest-strahlen frequency in cases like rock salt, sylvine, etc., could be satisfactorily connected with their ultra-violet absorption. It is interesting to note that the rule apparently fails in the case of diamond, which may be due to the fact that unlike the former cases of ionic lattices, diamond has a lattice built out of homopolar bonds.

7. *Relation to the Colour.*

It is suggested that the aggregate intensity of the bands and the continuous spectrum is responsible for the blue colour of diamonds. The attribution of this blue colour to the emission of such secondary radiations is not exceptional to diamond. A strikingly analogous case is that of crystalline anthracene which often exhibits a bluish-green tint due to fluorescence. Such a view for the origin of the blue in diamonds is very significant especially if it is recalled that the author has been able to photograph these bands as well as the continuous spectrum throughout the entire region even in reasonably clear and colourless diamonds, although their intensity is much less in comparison with the blue ones. This weakening in intensity of these secondary radiations with increasing clearness of the diamond, leaves it uncertain whether in the limiting ideal case of a colourless diamond the phenomenon would altogether disappear. For some reason it develops and attains a degree of prominence in particular samples resulting in a blue colour of sufficient intensity as to affect the eye ordinarily. The precise significance of the absorption frequencies of diamond in terms of its electronic structure is however not clear. The case of coloured rock salt is of interest in this connection as it is now known that the colour is not due to any contamination. Even the samples which are chemically pure show the phenomenon. In this case it is attributed to absorption of light by free neutral sodium atoms present in the lattice.

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[1] Verb d. D. Phys. Ges., Vol. 13, p. 1117 (1911).

[2] Born, *loc. cit.*

Finally, mention may be made here of an interesting property of diamond, *viz.*, its photoconductivity investigated in detail by Gudden and Pohl.[1] Their results show that every absorbed quantum of energy $h\nu$ liberates one electron. Such electrons are transferred to small distances by an external electric field and are responsible for the photoconductivity. Such an electronic disturbance must in some manner be related to the various other optical phenomena mentioned in this paper such as absorption, fluorescence, phosphorescence, Raman effect and colour. That Raman effect has also been classed amongst these need not be surprising if we recall here the views originally expressed by Sir C. V. Raman. The mechanism of the phenomenon as pictured by him essentially involves the electron, in that the incident light quantum tends initially to disturb the electron but its insufficient energy renders the attempt unsuccessful and results in a nuclear disturbance. Whether there is any real mutual relationship between the above phenomena and if so its precise nature, or if they are entirely independent and co-existing can only be decided with certainty after further experimentation.

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[1] Zeit. f. Phys., Vol. 17, p. 331 (1923).

In conclusion the author desires to express his best thanks to Prof. Sir C. V. Raman for suggesting the problem and giving many helpful suggestions in the course of the work. Grateful acknowledgments are also due to Sir Onkarmal Jatia, Mr. Nirmal Chunder Chunder, Mr. R. Ramjeedass Iyer, Messrs. Thakorlal Hiralal and Messrs. the Oriental Gem and Jewellery Co., whose kindness in loaning valuable diamonds made this investigation possible.

14

Raman Effect in some Crystalline Inorganic Sulphates.

Influence of Paramagnetism on Raman Lines

By

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(*Received for publication, 3rd July, 1930.*)

ABSTRACT.

Fifteen inorganic sulphates have been examined in the form of coarse crystals. The strong Raman line at about 10μ (ν_1) appeared in all cases except those of ferrous and nickel sulphates (heptahydrates). A weakening of the line with copper and manganese sulphates was also evident. This effect is attributed to the paramagnetic influence of the cations. In an aqueous solution of ferrous sulphate, however, the line appeared showing that the influence of the cation was very little in solution. A similar weakening also characterised the inactive NO_3 frequency in the paramagnetic nitrates of copper and manganese.

The shift in position of ν_1 for sulphates with cations in the same group of the periodic table follows their ionic size when similarly hydrated. The wave-lengths follow the order, NH_4, K, Na ; Ba, Sr, Ca ; Zn, Mg.

Of the other frequencies attributable to SO_4^{--}group, the one at about 22μ (ν_2) appeared as a somewhat diffuse line with NH_4, K, Ba, Cd and Hg sulphates. The third one at about 9μ (ν_3) was observed with K, Ca and Cd sulphates where it was faint. The fourth one at about 16μ (ν_4) was fainter and broader still and appeared with NH_4 and K sulphates. The last two frequencies (ν_3 and ν_4) agree with the two reflection maxima recorded by Schaefer and Schubert and hence are active frequencies while ν_1 and ν_2 which do not appear in the infra-red are probably inactive frequencies of the tetrahedral SO_4 group.

1. *Introduction.*

The present investigation is a continuation of the work of the author on crystalline powders of several inorganic [illegible] and chlorides.[1] The Raman spectra of a large number of sulphates have already been examined in aqueous solution[2] and a few in the form of single crystals[3] (*e.g.*, gypsum and barytes). It has been noticed that in the case of gypsum, the strong Raman line (1006 cm^{-1}) was considerably shifted from its position in the aqueous solutions of various sulphates (988 cm^{-1}). But the influence of the cation on the frequencies of the SO_4 group has not yet been systematically studied. Another point which requires study is about the intensities of the lines due to the SO_4 group and how far they are influenced by the surrounding field of cations in the 'rystal. The above points have been examined in some 'etail by the author with several inorganic nitrates where arge differences in the position of the inactive NO frequency 'ere observed with different cations.

Schaefer and Schubert have examined the infra-red spectra 'f a large number of sulphates and double sulphates by the eflection method.[4] They found two fundamentals at about)μ and 16μ in all cases which they attributed to the SO_4^{--} ion n the crystal, since they were found in all the sulphates. 'hey also found that in the uniaxial crystals each ındamental was doubled, the two components lying əry near together, and in bi-axial crystals, every fundaental was split up into three narrow components. The $)_4$ ion could be pictured as a regular tetrahedron with the atom at the centre and the oxygen atoms distributed at the ur corners. Brester[5] has examined the possible modes of bration of such a group and found them to consist of two intive (ν_1 and ν_2) and two active frequencies (ν_3 and ν_4). The ter only appear in the infra-red spectra and are probably əntical with the frequencies at 9μ and 16μ found by

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Krishnamurti, Ind. J, Phys., 5, 1, 113 (1930).

Nisi, Jap. J. Phys., 5, 119 (1929)

Krishnan, Ind. J Phys., 4, 131 (1929).

Schaefer and Schubert, Ann. d. Phys., 50, 283 (1916).

Brester, Dissertation, Utrecht, 1924

Schaefer and Schubert. The Raman spectra of the sulphates show all the four frequencies, the inactive ones coming out prominently, the one at about 10μ being the strongest both in aqueous solution as well as in the crystals. The average values obtained for the SO_4 frequencies in solutions of different sulphates as well as for gypsum and barytes are given below[0] in wave numbers.

TABLE I.

Frequency	Aq. Solutions	Barytes	Gypsum.
ν_1	983	984	1006
ν_2	447	452	484
ν_3	1115	1148	1132
ν_4	623	622	667

Table II gives the values for infra-red reflection obtained by Schaefer and Schubert.

TABLE II.

Sulphate of	Ca	Sr	Ba	Na	K	Cd	Cu	Ni
ν_3 in μ	8·74 8·62	8·84 9·05 8·35	8·73 8·30	8·72	8·82	9·02	9·20 9·13	9·01 8·96
ν_4 in μ	14·84	15·75	15·80	16·08	15·97	15·96	15·88	15·74

2. *Results.*

The substances which were of Merck's or Kahlbaum's origin were examined as such by the powder method. Barytes alone was examined as a single crystal. The sulphates of NH_4, K and Na were anhydrous. The following table gives the measurements for the strong Raman line at about 10μ in all cases, and for those at 9μ, 16μ and 22μ wherever observed. The wave-lengths of the lines obtained by linear interpolation from the nearest two known iron lines are given in I.A. units.

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[0] Taken from Nisi's paper, *loc. cit.*

TABLE III.

Exciting line, 4358. 34 I.A. (22938·1).

Frequency.	Sulphate of	Wave-length in I.A.	Δ ν in wave nos.	λ Wave-length in μ	Intensity.	REMARKS.
	Iron	...	...	...	...	Merck's reagent $FeSO_4$, $7H_2O$
	Nickel	...	...	...	...	Merck's pure $NiSO_4$, $7H_2O$
	Ammonium.	4551·62	973·9	10·268	Strong.	Kahlbaum's, for analysis$(NH_4)_2SO_4$
	Zinc	4552·34	977·5	10·230	,,	Merck's reagent. $ZnSO_4$. $7H_2O$
	Iron (soln.)	4552·46	978·3	10·222	Med. Str.	Nearly saturated at ord. temp.
	Copper	4552·84	979·7	10·207	Faint.	Kahl. 'for analysis' $CuSO_4$, $5H_2O$
	Potassium	4553·07	981·2	10·192	Strong	Merck's reagent K_2SO_4
	Magnesium	4553·29	982·1	10·182	,,	Kahl. $MgSO_4$, $7H_2O$
ν_1	Mercuric	4554·11	986·0	10·142	Med. Str.	,, $HgSO_4$
		4565·8	1042·3	9·594	,,	,,
	Barium	4554·42	987·5	10·127	Strong	Single crystal of Barytes $BaSO_4$
	Manganese	4554·59	988·4	10·117	Faint	Merck's $MnSO_4$, $4H_2O$
	Potash Alum	4554·93	989·9	10·102	Strong	,, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$
	Sodium (anhyd.)	4556·0	995·2	10·048	Med. Str.	, Na_2SO_4
	Strontium	4556·65	998·5	10·015	,,	Strontianite in small crystals $SrSO^4$
	Cadmium	4557·76	1003·8	9·962	Strong	Merck's Cd SO_4. 8/3 H_2O
	Calcium	4558·60	1007·7	9·924	,,	Gypsum crystals $CaSO_4$, $2H_2O$

Frequency.	Sulphate.	Wave-length in I.A.	$\Delta\nu$ in wave nos.	λ Wave-length in μ	Intensity.	REMARKS.
	Ammonium	4445·0	447	22·4	Faint	
	Potassium	4445·4	449	22·3	..	
	Barium	4446·5	455	22·0	Med. Str.	
ν_2	Pot. alum	4447	457	21·9	υ-faint.	
	Cadmium	4445	447	22·4	..	
	Iron	4432	381	26·2	υ-faint diffuse.	Doubtful.
	Mercuric	4455·2	499	20·0	Med. Str.	
	Calcium	4583·5	1127	8·87	Faint diffuse.	
ν_3	Potassium	4587	1143	8·75	υ-faint, sharp.	Faint indications of a companion on either side.
	Cadmium	4582	1129	8·93	υ-faint, diffuse.	
	Ammonium	4480·1	623	16·05	Faint, diffuse	
ν_4	Potassium	4479·1	618	16·18	..	
	Iron	4490	673	14·86	υ-faint, diffuse.	Doubtful.

3. *Discussion of Results.*

The striking fact emerges out of this investigation that *in ferrous and nickel sulphates, especially the former, the Raman line corresponding to 10μ is so weak that it is not possible to* observe it on the plate. Several exposures were given for ferrous sulphate which was of Merck's reagent quality and consisted of fairly large, transparent crystals. Two very faint bands at shorter wave-lengths were seen on the plate, but no trace of the 10μ frequency could be observed. Somewhat longer exposures had to be given for ferrous sulphate (about 4 hrs.) on account of its pale green colour. The incident line was well exposed on the plate as well as the continuous background accompanying it. Nickel sulphate was not so well-exposed since the crystals were of deeper colour. These two sulphates are exactly those which possess a large paramagnetic susceptibility, and the intrinsic magnetic field due to the cation is obviously responsible for the extreme weakness or absence of the 10μ line which appears strongly with all the other diamagnetic sulphates. This idea receives support when we consider the intensities of the same line in the other two paramagnetic sulphates examined, *viz.*, those of copper and manganese. The crystals were large and quite transparent, but the 10μ line appeared only feebly on the plate and was just measurable, while the lines obtained with magnesium, zinc and the alkali sulphates were quite strong.

In the case of ferrous sulphate, a nearly saturated aqueous solution was examined. It showed the 10μ line in the usual position, indicating thereby that the influence of the Fe^{++} ions was not very marked in solution. This suggests that the magnetic effect ought to increase with decreasing amount of water in the crystals, attaining a maximum with anhydrous crystals. This seems to be so at least in the one case of copper nitrate studied by Gerlach[1] in which he does not find the inactive NO_3 frequency in the anhydrous salt.

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[1] Gerlach. Ann. d. Phys., 5, 196 (1930).

A similar diminution of intensity of the NO_3 frequency ($9{\cdot}5\mu$) with manganese and copper nitrate crystals has been observed by the present author,[1] while the other nitrates usually gave very strong Raman lines.

The infra-red reflection spectrum of $FeSO_4, 7H_2O$ has not been studied by Schaefer and Schubert. They have, however, studied $NiSO_4, 6H_2O$ which shows broad and very faint maxima at 9μ and $15{\cdot}7\mu$. From their curves it will be evident that the peaks are lower and broader than those with any other sulphate examined by them.

We now come to consider the influence of the cation in shifting the position of the prominent SO_4 frequency at about 10μ. The influence of the Ca^{++}ion is very large as has already been pointed out by other observers. Among elements of the I group of the periodic table, the frequencies of the anhydrous salts show smaller shifts with increasing volume of the cation, *e.g.*, Na, 995 cm^{-1} ; K, 981; NH_4, 974. In group II the same change occurs, Ca, 1008 ; Sr, 999 ; Ba, 988 cm^{-1}. The value for anhydrous $CaSO_4$ ought to be even greater than in the hydrate by comparison with the nitrates.[2] In the same group, magnesium and zinc sulphates are comparable since they are isomorphous and similarly hydrated, and here also we find the same change, Mg, 982 cm^{-1}; Zn, 978, consistent with the fact that the latter comes after magnesium in the periodic table. Mercury shows two lines, one of which has the normal value, and the other corresponds to the frequency observed for the HSO_4 group. (1050 cm^{-1}).

With regard to the other frequencies, we can first take the one at about 22μ (ν_2) for consideration. This has also no analogue in the infra-red, but it is usually weaker than ν_1. In the present experiments it was observed with fair intensity in the case of K, NH_4 and Ba sulphates. The values were not very different from each other nor from the value found in solutions of other sulphates. This line, unlike that due to ν_1, is fairly diffuse and is never sharp. This is probably connected with the fact that it is due to a double oscillation while ν_1 is due to a single oscillation.

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[1] Krishnamurti, *loc. cit.*

[2] Gerlach, *loc. cit.*

The third frequency (ν_3) occurs at about 9μ in K, Ca and Cd sulphates. In the last two cases, it is diffuse whereas in K_2SO_4 it is sharp though faint and seems to be accompanied by a still fainter companion on either side. This is probably because it is a biaxial crystal, and represents 'trichroism' as found in the infra-red for strontium sulphate crystals.[1] ν_3 is an active frequency and its values agree fairly with those found by Schaefer in the infra-red. The fourth frequency ν_4 also observed in the infra-red and hence active occurs at about 16μ in both cases. The lines wherever observed (*K* and NH_4 sulphates) were weaker and more diffuse than the one at 22μ (ν_2).

Finally, the relative intensities of the four frequencies deserves mention. The inactive frequency ν_1 comes first in order of intensity and next comes ν_2 in most of the sulphates. In K_2SO_4 where all the four lines were observed, $\nu_1 > \nu_2 > \nu_4 > \nu_3$. The relative intensities are not however the same in all cases, and in a dilute solution ν_1 is the strongest, and all the other three equally weak and diffuse. In the tetrahedral model suggested for the SO_4 group, ν_3 and ν_4 (9μ and 16μ) which appear in the infra-red reflection are taken as active frequencies while ν_1 and ν_2 (10μ and 22μ) as inactive ones since they are not reported in the infra-red. This view has also been adopted by Schaefer in a recent paper.[2] However, the variable nature of the positions and intensities of the lines (within certain limits) with different cations shows that the SO_4 group is easily deformable and that it may depart from tetrahedral symmetry to a considerable extent.

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[1] Schaefer and Schubert, *loc. cit.*

[2] Schaefer, Z. f. Phys., 60, 587 (1930).

4. *Conclusion.*

These investigations on crystals bring to light the essential dependence of the Raman frequencies on physical conditions, *e.g.*, when hydrated, in solution, the size of the surrounding ions, and what seems very important, on the magnetic fields exerted in the neighbourhood of the anion by the paramagnetic cation. It has already been shown by the author that the Raman frequencies corresponding to the polar groups are most influenced by a change from the solid to the liquid state.[1] It seems very likely in view of all these facts that the Raman lines might undergo modifications in the presence of strong electric or magnetic fields especially when polar groups are present, and work on these lines is in progress.

The author's best thanks are due to Professor Sir C. V. Raman, F.R.S., for his inspiring guidance in this investigation.

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[1] Krishnamurti, Nature, March 22, p. 463 (1930).

15

Raman Spectra of Inorganic Sulphates and Nitrates

By

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(*Received for publication, 20th July 1930.*)

ABSTRACT.

Raman spectra of aqueous solutions of several inorganic sulphates and nitrates have been obtained. The three bands due to water appear in all cases in approximately similar positions ($\Delta\nu=3630$, 3440 and 3180 cm^{-1}). The sulphates show four frequencies attributable to the SO_4 ion ($\Delta\nu=457$, 617, 981 and 1102 cm^{-1}), the first and third being inactive and the other two active frequencies. The nitrates give three lines due to the NO_3 ion ($\Delta\nu=726$, 1048 and 1357 cm^{-1}), of which the middle one is the inactive and the other two active frequencies, the latter appearing also in the infra-red spectra. It is shown that the frequencies observed in the sulphates and nitrates are fundamental and characteristic of the respective ions. *An explanation is suggested for the large intensity of the inactive frequencies in the Raman spectra.*

I. *Introduction.*

As first pointed out by Prof. Raman,[1] the wave-number shifts of the modified lines in the scattered spectrum correspond to the *actually existent* characteristic frequency of the molecule. This has been further confirmed by the work of Bhagavantam and Venkateswaran[1] on Raman effect in organic halogen compounds. The exact confirmation of this idea can only however be testified by the investigation on simple molecules or groups (like SO_4, NO_3, etc.).

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[1] C. V. Raman, Ind. Jour. Phy., Vol. 2, pp. 387, 399 (1928).

Further in such simple cases like SO_4, NO_3, CO_3 where the vibrational frequencies are theoretically calculable from the geometry of their structure, some of them are optically inactive, *i.e.*, the corresponding vibrations involve no alteration in the electric moment. Indeed it has been pointed out by Carrelli, Pringsheim and Rosen,[2] that in the case of NH_4NO_3, HNO_3, $NaNO_3$, solutions, the observed lines (wave-number shift of 1045) corresponded to the inactive frequency of the nitrate group.

It has also been pointed out by some observers,[3] that the wave-number shifts corresponding to certain groups were not quite identical, when the substance investigated was either in a crystalline state or in solution.

It was with a view to understand these aspects of the subject further that the present work was undertaken. The present paper deals with a number of inorganic simple salts containing the nitrate or the sulphate groups, both in the solid crystalline state, as well as in aqueous solution.

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[1] S. Bhagavantam, and S. Venkateswaran, Roy. Soc. Proc. A. Vol. 127, p. 364 (1930).

[2] A. Carrelli, P. Pringsheim and B. Rosen, Zeit. fur. Physik, Vol. 51, p. 511 October, 1928.

[3] *Note by Editor, dated 25th July, 1930* :—Reference may be made to the following papers which have appeared recently. The author's work was evidently done independently, and contains important new results.

Dickinson and Dillon, Proc. Nat. Acad. Sci., *15*, 334 and 695 (1929).
Nisi, Jap. J. Phys., 5, 119 (1929).
Kishi, Mem. Coll. Sci., Kyoto, *13*, 163 (1930).
Krishnamurti, Ind. J. Phys., 5, 1 (1930).
Gerlach, Ann. d. Phys., 5, 196, (1930).

II. *Experimental.*

(Aqueous solutions.)

Such of the salts as were readily soluble in water, and were not hydrolysable were first used in the state of solution. Pure distilled water was used as the solvent. The salts were all Kahlbaum's chemicals ; these were further purified by re-crystallisation, wherever possible. A saturated solution was first made, and then rendered comparatively dust-free by careful repeated filtration. As no other simple method of preparing the solution free from suspended impurities was available, this method had to be resorted to. Further it was found that the Raman spectra obtained for these solutions, were not materially improved by adopting more stringent measures for purification.

For photographing the Raman spectra of these solutions, the method adopted was essentially that of Wood.[1] The apparatus is too well-known to be described here in detail.

The solution was put in the tube, water was circulated in the outer jacket, by connecting it to a tap. The quartz-mercury lamp which was used, was of a design (Z2B type) that could not be brought quite close to the Wood's tube and still be parallel to the length of the solution. It was therefore kept at as little inclination as possible consistent with its nearness to the tube.

The method of aiming the spectrograph was exactly the same as that of Wood.[2] This was found to be quite necessary, as otherwise the exposures were unnecessarily lengthened.

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[1] R. W. Wood, Phil. Mag., Vol. 6, p. 729, October, (1928).

[2] Wood (*loc. cit.*).

One of the chief difficulties in the use of the mercury-arc was the presence of the continuous back-ground in the incident mercury spectrum. This continuous spectrum scattered by the solution made the weaker lines barely detectable. It was found that this was much reduced by running the arc at a comparatively low temperature by directing a gentle blast of air against it, by means of an ordinary table-fan, though it necessitated longer exposures.

With this arrangement, using Ilford Iso-Zenith (speed No. 700 H. D.) plates and a small Hilger constant deviation glass spectrograph, an exposure of 4 hours was found to give a satisfactory spectrogram. The photographic plates were backed before use, by attaching to the glass-side a black paper wetted with glycerine.

The plates were all measured on a Hilger micrometer, and the wave-lengths of the lines calculated by using the simplified form of Hartmann's interpolation formula, with the known mercury lines appearing on the plates as standards. The wave-numbers of the lines (in vacuo per cm.) were then calculated, and the shift in wave-numbers of the Raman lines from the corresponding exciting lines determined. Under the column $\Delta\nu$ are given the difference between the wave-number of Raman lines, and the exciting lines of the mercury spectrum λ A. U. 3650·1, 3654·8, 3663·3, 4046·6, 4077·8, 4108·9, 4339·2, 4347·5, 4358·3, respectively by the letters a, b, c, d, e, f, g, h and k respectively. Such of the Raman lines which happen to coincide with the incident lines of the mercury spectrum are not included in the tables.

TABLE I.

Solutions of Sulphates.

Sodium	Potassium	Ammonium	Magnesium	Zinc	Cadmium	Aluminium	Assignment
......	......	......	19505 (3)	......	19520 (2)	......	$k-S_2$
21040 (4)	21063 (4)	......	21064 (4)	21106 (4)	21079 (4)	21072 (4)	$d-S_1$
21252 (4)	21268 (4)	21264 (4)	21264 (4)	21279 (4)	21300 (4)	21252 (4)	$d-S_2$
21490 (2)	21554 (2)	21503 (2)	21541 (2)	21554 (2)	21539 (2)	21566 (2)	$d-S_3$
21837 (0)	21848 (0)	21834 (0)	21826 (0)	21837 (0)	21837 (0)	21834 (0)	$k-S_7$
21956 (4)	21958 (4)	21957 (4)	21955 (4)	21955 (4)	21954 (4)	21957 (4)	$k-S_4$
22324 (1)	22318 (1)	22320 (1)	22322 (1)	22320 (1)	22319 (1)	22324 (1)	$k-S_6$
22478 (2)	22481 (2)	22481 (2)	22479 (3)	22482 (2)	22481 (2)	22481 (2)	$k-S_5$
......	......	......	23399 (0)	......	......	......	$k+S_5$
23533 (2)	......	23533 (1)	23532 (2)	23533 (2)	23533 (2)	......	$e-S_4$
23725 (4)	23722 (4)	23727 (4)	23722 (4)	23723 (4)	23725 (4)	23725 (4)	$d-S_4$
23748 (4)	23785 (4)	......	23760 (4)	23793 (4)	23782 (4)	23780 (4)	$a-S_1$
23927 (4)	23920 (4)	23921 (4)	23938 (4)	23941 (4)	23939 (4)	23950 (4)	$a-S_2$
24088 (2)	24087 (1)	24095 (1)	24087 (2)	......	......	......	$d-S_6$
......	24160 (1)	......	......	24154 (2)	24164 (2)	24189 (2)	$a-S_3$
24245 (2)	......	24226 (1)	24255 (1)	......	24251 (2)	......	$d-S_5$

TABLE II.

Abstract Table—Sulphate Solutions.

	H_2O frequencies			SO_4^{--} frequencies			
Sulphate of ...	S_1	S_2	S_3	S_4	S_5	S_6	S_7
Sodium ...	3653	3457	3179	981	460	615	1101
Potassium ...	3623	3453	3190	981	457	619	1090
Ammonium ...	......	3454	3182	980	457	614	1104
Magnesium ...	3635	3442	3149	983	460	617	1112
Zinc ...	3598	3437	3194	982	456	618	1101
Cadmium ...	3616	3424	3195	982	455	619	1101
Aluminium ...	3620	3446	3170	980	457	614	1104
Average value ..	3630	3440	3180	981	457	617	1102

TABLE III.

Solutions of Nitrates.

Sodium	Potassium	Ammonium	Calcium	Strontium	Barium	Lead.	Assignment
19521 (2)	....	....	......	....	19488 (2)	....	$k-n_2$
21060 (3)	21070 (3)	21066 (3)	21084 (3)	21060 (3)	21041 (3)	21075 (3)	$d-n_1$
....	21275 (3)	21277 (3)	21217 (3)	21275 (3)	21304 (3)	21321 (3)	$d-n_2$
21549 (3)	21498 (1)	21517 (2)	21500 (2)	21497 (2)	21545 (2)	21514 (2)	$d-n_3$
....	....	....	......	21570 (0)	....	....	$k-n_4$
21887 (6)	21888 (6)	21889 (6)	21888 (6)	21888 (6)	21888 (6)	21891 (6)	$k-n_5$
22213 (1)	22208 (2)	22210 (2)	22218 (2)	22210 (2)	22228 (2)	22208 (2)	$k-n_6$
23275 (0)	....	....	... ..	23275 (0)	23288 (0)	....	$f-n_5$
23344 (0)	23348 (0)	23344 (0)	......	23344 (0)	23355 (0)	....	$d-n_4$
23464 (2)	....	....	......	23467 (2)	23465 (2)	23468 (2)	$e-n_5$
23657 (6)	23657 (6)	23657 (6)	23657 (6)	23655 (6)	23658 (6)	23657 (6)	$d-n_5$
23733 (4)	23752 (4)	23733 (4)	23821 (4)	23752 (4)	23751 (4)	23769 (4)	$a-n_1$
23894 (4)	23971 (4)	23969 (4)	23934 (4)	23971 (4)	23910 (4)	23944 (4)	$a-n_2$
23985 (2)	....	....	......	....	23985 (2)	....	$d-n_6$
24157 (2)	24222 (2)	24250 (2)	24254 (2)	24146 (2)	24222 (2)	24153 (2)	$a-n_3$
26245 (0)	26242 (0)	26244 (0)	26243 (0)	26245 (0)	26243 (0)	26245 (0)	$c-n_5$
26303 (2)	26303 (2)	26303 (2)	26303 (2)	26303 (2)	26295 (2)	26304 (2)	$b-n_5$
26342 (3)	26342 (3)	26342 (3)	26339 (3)	26342 (3)	26341 (3)	26342 (3)	$a-n_5$

TABLE IV

Abstract Table—Nitrate Solutions

	H_2O frequencies			NO_3^- frequencies		
Nitrate of ...	n_1	n_2	n_3	n_4	n_5	n_6
Sodium ...	3650	3456	3161	1361	1048	725
Potassium ...	3636	3424	3187	1357	1049	730
Ammonium ...	3647	3424	3163	1361	1047	728
Calcium ...	3594	3471	3170	—	1048	720
Strontium ...	3641	3424	3225	1354	1049	728
Barium ...	3647	3443	3162	1350	1049	720
Lead ...	3625	3414	3213	—	1047	730
Average value. ...	3630	3440	3180	1357	1048	726

An examination of the tables II and IV shows.

(1) That all the solutions studied, reveal the presence of the three diffuse bands characteristic of water, with mean wave-number shifts 3630, 3440, 3180 respectively, the central band being the strongest of the three. These wave-number shifts are in satisfactory agreement with the wave-number shifts for pure water given by A. S. Ganesan and S. Venkateswaran.[1]

(2) The solutions of all sulphates give Raman lines corresponding to mean wave-number shifts of 1102, 981, 617, and 457. These four persist to have the *same* value in *all* the solutions (within the limits of errors of measurements), and are independent of the nature of the free cation in solution.

(3) The solutions of all nitrates give apart from the water bands lines corresponding to wave-number shifts of 1357, 1048

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[1] A. S. Ganesan and S. Venkanteswaran, Ind. Jour. Physics, Vol. IV, Part III, p. 237, (August, 1929).

and 726; these are, as in the case of sulphates, attributable to the NO_3 ion, and persist to have the same value in all the nitrates in solution, independent of the nature of the cation in solution.

III. *Raman Effect in Powdered Crystals.*

The influence of the cation on the oscillations of the NO_3 or SO_4 group, was however observed, when the substance investigated was in the solid crystalline state. Only a preliminary study has so far been made in this direction, in the case of aluminium nitrate.[1] Coarse crystals of aluminium nitrate were confined between two plates of glass (with mirrored walls), kept inclined to each other, so as to form a triangular cell. The mercury arc was brought as close to the crystals as was possible, and parallel to the length of the cell. The scattered light from the crystals, was focussed on to the slit of a glass spectrograph. Direct light from the arc was avoided from entering the spectrograph, with the help of suitable diaphragms. Due to the unavoidable presence of much reflected light from the crystals and the continuous back-ground of the mercury spectrum, the strong back-ground in the photograph rendered it difficult to measure accurately the weaker lines. But the two strongest lines (excited by 4046·6 and 4358·3) those corresponding to 1048 wave-numbers in the solutions, could be accurately measured, and wave number shifts were found to be 1056. Considering the intensity and sharpness of the line, the difference of wave numbers from the value for the corresponding shift in the case of the nitrates in solution is too large to be attributed to errors of measurement. It appears therefore, that the cation has a *definite* influence on the oscillations within the anion, in the crystal lattice. Reference should be made in this connection to a recent interesting note by P. Krishnamurti.[2]

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[1] A more extensive study of this aspect is in progress.

[2] P. Krishnamurti, Nature, March 22, 1930.

IV. *Relation to Ionic Structure.*

Let us first take the case of sulphates and discuss the above-obtained results from the point of view of the structure of the SO_4 group.

Following David M. Dennison[1] in his discussion on the structure of the methane molecule, we can picture the SO_4 group in the normal state as a perfect tetrahedron, the four oxygen atoms lying at the corners while the sulphur atom lies at the centroid.

The Raman lines under the conditions of dispersion employed were sharp, and showed no structure, indicating that all the four bonds connecting the oxygen atoms to the sulphur are alike. A study of the Raman spectra of these solutions, with a much higher dispersion is however necessary, to decide otherwise.

Assuming the amplitudes of the vibration to be infinitesimal and that the fields of force possess a central symmetry about each particle, Dennison[2] shows that four *fundamental* frequencies ν_1 ν_2 ν_3 and ν_4 may be absorbed, two of them very faintly, two very intensely.

Dennison further shows that the intensity of ν_1 ν_2 should be theoretically zero, and the small intensity of the infra-red bands actually observed, is a measure of the errors involved in considering the motions to be infinitesimal.

ν_1 and ν_2 therefore correspond to vibrations which, to a first approximation, do not involve any alteration in the electric moment of the group as a whole, and therefore represent the *optically inactive* frequencies.

Now, the strongest Raman line of the SO_4 ion. corresponds to a mean wave-number shift of 981, the next in intensity

David M. Dennision, Astrophysical Journal, Vol. 62, p. 84 (1926.)

David M. Dennison, *loc. cit.*

corresponding to a mean wave-number shift of 457. These two frequencies have not so far been observed *directly* in the *infra-red.* The explanation for the appearance of the inactive frequencies as Raman radiations suggested in the following section, indicates that these two frequencies correspond to inactive fundamental oscillations in the SO_4 group.

Now Dennison[1] gives for the inactive frequencies the expressions

$$\nu_1 = \frac{1}{2\pi} \sqrt{\frac{k_2}{m}(4a+1)}$$

$$\nu_2 = \frac{1}{2\pi} \sqrt{\frac{k_2}{m}\left(a - \frac{\beta}{4}\right)}$$

m = mass of hydrogen atom in the case of CH_4 molecule.

The ratio of the two frequencies (ν_1/ν_2) is roughly 2 (neglecting 1 in comparison with $4a$, and $\beta/4$ in comparison with a which is justifiable). The ratio of the two wave-number shifts 981 and 457 obtained in our experiments is approximately 2·1 and the agreement between the two ratios must be taken as lending support to the view presented above.

Further the statement, that the four frequencies observed may be regarded as two of them being fundamentals and the other two as combinational or overtone frequencies, seems to be untenable.[2]

Thus if the lines corresponding to wave-number shifts 981 and 616 be regarded as fundamentals ν_2' and ν_1' and the 457 and 1102 frequencies be regarded as ν_2' ν_1' and $2\nu_1'$ respectively, the actual values of ν_2'-ν_1' and $2\nu_1'$, differ from 457 and 1102, by amounts which are too large to be allowable even as being due to the anharmonic nature of the oscillations.

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[1] See in this connection Dennison's paper (*loc. cit.*)

[2] See in this connection A. M. Taylor, Faraday Society discussion "On Molecular Spectra." (Bristol Meeting, 1929.)

Thus it appears that all the four frequencies observed in the case of the SO_4 ion are pure fundamental oscillations, two of them active—which have been observed in the infra-red—and the two inactive—which are only detectable as Raman radiations.

Let us now take the case of the NO_3 group. The NO_3 group is quite analogous to the CO_3 group, the vibrations corresponding to which have been worked out in detail, by Kornfeld.[1] We can picture the nitrate ion as an equilateral triangle in which the oxygen atoms occupy the vertices, the nitrogen being situated in the centroid. The oscillations in every case, due to the greater weight of nitrogen (relative to carbon), are slower than the corresponding oscillations in the CO_3 group.

As has been pointed out by C. A. Carrelli, Peter Pringsheim, and B. Rosen,[2] the strongest line (the only one observed by them) with a wave-number shift of 1048 corresponds to the known optically inactive frequency for the NO_3 ion.

The other two frequencies corresponding to wave-number shifts 1357 and 726, correspond to the *active* oscillations and have been directly observed in the infra-red.

The inactive oscillation (1048 wave-number shift), corresponds to the symmetric expansion and contraction of the NO_3 group as a whole, the centre of gravity of the negative charges (oxygen) remaining at the centroid, being superimposed upon the positively charged nitrogen.

The vibration corresponding to the wave-number shift 726 is caused by drumhead vibration of the ion, the nitrogen oscillating perpendicularly to the plane of the triangle. The vibration corresponding to the wave-number shift 1357 (in analogy to the case of the CO_3 group) can be attributed to the oscillation of the nitrogen in the plane of the triangle, along or perpendicular to any median, the remainder of the group being considered rigid, to a first approximation.

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[1] Kornfeld, Zeit. fur. Physik, Vol. 26, 205, (1924).

[2] A. Carrelli, P. Pringsheim, and B. Rosen, Zeit. fur. Physik., Vol. 51, p. 511, October, 1928.

All these observed Raman frequencies correspond to fundamental oscillations, active or inactive.

V. *Optically Inactive Frequencies.*[1]

The question still remains as to why the optically inactive frequencies appear strongly in the scattered spectra. An explanation of this can be given on lines similar to those given by Rasetti.[2]

The fact that the vibrational transitions in N_2 and O_2 show no rotational structure though theoretically the transitions $m \rightarrow m-2$, $m \rightarrow m$, $m \rightarrow m+2$ (m=rotational quantum number) are possible is explained by Rasetti as follows. If m remains unchanged, the position of the lines is nearly independent of m, and therefore, all the transitions $m \rightarrow m$, has a very high "statistical weight" *i.e.*, if after the excitation by the incident line, the *rotational state* is unchanged, that particular transition has more than usual probability.

Also Van Vleck has shown that the lines corresponding to $\Delta v=0$ representing the simple Rayleigh scattering are most intense.

From the above it appears *that those lines appear most strongly in the Raman effect, which are consequent to the least disturbance after the excitation*[3]—$\Delta m=0$ in rotation, giving the vibration-line without the rotational structure, and $\Delta v = 0$ giving the Rayleigh scattering. Thus, generalising, that transition which involves no alteration in the electric moment after the excitation, should have an unusually high "statistical weight." Thus we have a qualitative explanation as to the strong appearance of the inactive frequencies in the Raman effect.

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[1] This section was written in collaboration with Mr. S. Chandrasekhar, and the author wishes to acknowledge his great indebtedness to him for the same.

[2] Rasetti, Nature, Vol. 123, p. 757, 1929.

[3] It *does not necessarily* follow that (all) the weak lines of the infra-red should come out strong in the Raman-effect.

In conclusion, I have great pleasure in expressing my most sincere and heart-felt thanks to Dr. H. Parameswaran, for his constant encouragement and interest during the whole course of this work.

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Raman Spectra under High Dispersion.

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(Plate X)

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ABSTRACT.

Raman spectra of benzene, chloroform and carbon-tetrachloride are studied using a high dispersion spectrograph. The benzene 3μ band is observed to split up into five different components. Two new lines 22516·2 cm^{-1} and 22743·3 cm^{-1} are observed on the benzene plate, their probable assignment is given as 2188 cm^{-1} and 1961 cm^{-1} due to λ4046 excitation. A new frequency 3072·4 cm^{-1} is reported for chloroform along with the 3017·3 cm^{-1} already reported by previous workers. Details of the spectral characters of the various Raman lines of these liquids are recorded. A winged nebulosity is observed accompanying the unmodified Hg lines in benzene. This appears with reduced breadth in chloroform, but is hardly noticeable in CCl_4.

1. *Introduction.*

Since the discovery of the Raman effect early in 1928, a large mass of data on the subject has been published, but very few workers have so far examined the Raman spectra of substances under high dispersion. Wood [1] was the first to make a high dispersion study of the Raman spectra of benzene and carbon-tetrachloride by using a 6 inch plane grating with a lens of three metres focus. In a recent investigation Langer and Meggers [2] have also employed a grating spectrograph to study a few common substances. The only satisfactory examination, however, seems to have been done by Söderqvist [3] who used a two-prism spectrograph with a high dispersion, and has observed some interesting results in the case of benzene, the most frequently studied liquid.

The present investigation was undertaken to study the Raman spectra of some typical common substances, under fairly high dispersion. For this purpose a Hilger quartz E_1 spectrograph having a dispersion of 13 A.U. per mm. at λ4000 was very kindly placed at the disposal of the author by Prof. Sir C. V. Raman. The instrument was set up for the visible region as only glass containers were used for the liquids studied. Wood's arrangement was followed to get the scattered light. Even with the best conditions of illumination the spectrum observed visually was far too weak to show any thing but the incident Hg line λ4358. Consequently prolonged exposures of 24-36 hours had to be given to get fairly well-exposed plates using Isozenith plates. To make the instrument least susceptible to the thermal variations of the atmosphere during such long periods of exposures, all the exposed parts of the instrument were carefully covered by quilt pieces.

A comparison spectrum from an iron arc was recorded on each plate. The plates were measured on a Hilger cross-slide photo-measuring micrometer reading up to 0·001 mm. Wave-lengths were computed by linear interpolation between close iron lines not more than 15-20 A. U. apart, or by Hartmann's interpolation formula, taking suitable iron lines as standards. Very faint and diffuse lines that could not be seen clearly under the high magnification of the measuring instrument, were visually estimated correct to one Angstrom unit.

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[1] Wood, Phil. Mag. VI, p. 1282 (1928).

[2] Langer and Meggers, Jour. Bur. Stand., 4, p. 711, (1930).

[3] Söderqvist, Z. f. Phys. 59. p. 446 (1930).

2. *Results.*

The Raman spectra of benzene, chloroform and carbon-tetrachloride are studied and the results are given in tables I-III. The first two columns give the intensities and wave numbers in vacuo per cm. of the Raman lines observed. The third gives the frequency shifts or the Raman-frequencies $\Delta\nu$ in vacuo per cm., the letters *a*, *b*, *c*, etc., denote the various exciting Hg lines according to the lettering given in the following table.

Table IV—Hg arc in vacuo.

	λ in A.U.	ν vac. per cm.		λ in A.U.	ν vac. per cm.
a	3650·14	27388·5	*e*	4077·84	24515·7
b	3654·83	27353·4	*f*	4339·25	23038·7
c	3663·27	27290·3	*g*	4347·50	22994·9
d	4046·80	24703·8	*h*	4358·34	22937·8

The results of some of the previous workers and of the present investigation are given in the comparative tables V-VII. It will be seen that the agreement between the various values is quite good.

TABLE I. Benzene.

Raman lines.		Δν	Raman lines.		Δν
I.	Wave numbers in vacuo per cm.		I.	Wave numbers in vacuo per cm.	
2	19811·3	g−3183·6	0d	22516·2	?
2	19876·5	h−3061·3	0d	22743·3	?
1B	19894·1	h−3043·7	1	23096·7	d−1607·1
1	19984·3	h−2953·5	1	23120·0	d−1583·8
1	21330·2	h−1607·6 e−3185·5	1	23341·4	e−1174·8
1	21354·7	h−1583·1 e−3161·0	5	23523·5	d−1180·3 e−992·2
			10	23713·3	d−990·5
0	21456·2	e−3059·5	0	23859·1	d−844·7
0B	21463·3	e−3052·4	0	23914·0	e−601·7
0	21521·7	d−3182·1	0	23927·7	h+989·9
0	21543·2	d−3160·6	2	24100·4	d−603·4
0	21561·8	e−2953·9	0	24126·5	c−3163·8
5B	21641·7	d−3062·1	2	24169·4	b−3184·0
2B	21656·1	d−3047·7	2	24203·6	a−3184·9
3	21758·2	h−1179·6 d−2946·6	4	24226·5	a−3158·0 c−3063·8
10	21945·1	h−992·7	4	24289·4	b−3064·0
1	22002·5	g−992·4	0	24304·3	b−3049·1
0	22049·0	f−989·7	1	24323·7	a−3064·8
1	22085·1	h−852·7	1	24403·2	b−2950·2
3	22332·3	h−605·5	1	24437·8	a−2950·7

Raman-frequencies of benzene.—

{ Δν——3184·0 (2), 3160·5 (0), 3062·3 (4), 3048·5 (1B), 2950·8 (2).
{ λ in μ——3·140, 3·163, 3·265, 3·279, 3·388.

Δν——1607·4 (1), 1583·4 (1) 1178·1 (1), 991·2 (8), 848·7 (0), 603·9 (2).
λ in μ——6·219, 6·314, 8·486, 10·09, 11·88, 16·55.

TABLE II. Chloroform.

Raman lines.		Δν	Raman lines.		Δν
I.	Wave No. in vacuo per cm.		I.	Wave No. in vacuo per cm.	
1	19920·5	*h* −3017·3	0	23260	*g* + 265 *d* − 1444
0d	21445·5	*e* −3070·2			
1	21499·8	*e* − 3015·9 *h* − 1438·0	1	23302·4	*h* + 304·6 *e* − 1213·3
0d	21628·7	*d* − 3075·1	0	23492·0	*d* − 1211·8
4	21685·8	*d* − 3018·0	1	23609·9	*h* + 672·1
2	21723·0	*h* − 1214·8	0B	23749·5	*e* − 766·2
0	21780	*g* − 1214	1	23848·5	*e* − 666·2
3V.B	22179·1	*h* − 758·7	2V.B	23944·5	*d* − 759·3
0V.B	22231	*g* − 763	5	24039·1	*d* − 664·7
8	22269·3	*h* − 668·5	2	24148·3	*e* − 367·4
1	22332·3	*g* − 662·6	0d	24218	*c* − 3072
0	22374·3	*f* − 664·4	1B	24254·4	*e* − 261·3
6	22571·1	*h* − 366·7	1B	24274·4	*c* − 3015·9
1	22628·6	*g* − 366·3	3	24369·1	*a* − 3019·4
5	22677·5	*h* − 260·3	3	24966·4	*d* + 262·6
0	22730·1	*g* − 264·8	2	25073·5	*d* + 369·7
2	23203·3	*h* + 264·6	1	25376·1	*d* + 672·3

Raman frequencies of chloroform:—

Δλ——3072·4 (0d), 3017·3 (2). 1441·0 (1), 1213·5 (2).
λ in μ—3·254, 3·313, 6·937, 8·253.

Δν——761·8 (3B), 667·2 (6). 366·9 (5), 263·3 (4).
λ in μ—13·12, 14·98, 27·25, 38·11.

TABLE III. Carbon tetrachloride.

Raman Lines		Δν		Raman Lines	Δν
I	Wave No in vacuo per cm.		1	Wave No in vacuo per cm.	
0d	21403	*h* − 1535	0	23314	*g* + 319 ?
2d	22147·9	*h* − 789·9	1	23397·1	*h* + 459·3
2d	22177·6	*h* − 760·2	2d	23912·3	*d* − 791·5
10	22476·1	*h* − 461·7	2d	23941·2	*d* − 759 6
0	22539·8	*g* − 455·1	2	24051·7	*e* − 464·0
8	22621·2	*h* − 316·6	0	24200·5	*e* − 315·2
0	22676·0	*g* − 318·9	5	24244·1	*d* − 459·7
6	22718·4	*h* − 219·4	0	24297·5	*e* − 218·2
0	22775·9	*g* − 219·4	3	24387·8	*d* − 316·0
1	23119·2	?	3	24486·0	*d* − 217·8
4	23154·6	*h* + 216·8	1	24923·0	*d* + 219·2
1	23208	*g* + 213	0	25016·5	*d* + 312·7
2	23252·0	*h* + 314·2	0	25162·5	*d* + 458·7

Raman frequencies of Carbontetrachloride—

{ Δν—1535 (*0d*), 790·7 (*2d*), 759·9 (*2d*), 459·7 (6), 315·6 (4), 217·7 (4).
{ λ in μ—6·512, 12·64, 13·16, 21·75, 31·68, 45·92.

TABLE V. Raman frequencies of benzene.

Raman[4] and Krishnan	Wood[5]	Pringsheim[6] and Rosen	Dadieu[7] and Kohlrausch	Soderqvist	Langer and Meggers	Author.
...	266·2	...	...	...	...	...
605 (1)	606·3	615 (3)	604 (4)	604·6 (2)	605·7	603·9 (2)
849 (0)	847·9	867 (2)	846 (2)	849·1 (0)	848·6	848·7 (0)
991 (10)	989·7	995 (4)	994 (10)	991·3 (5)	992·1	991·2 (8)
1176 (2)	1170·2	1183 (3)	1174 (3)	1179·0 (1)	1177·3	1178·1 (1)
...	...	...	1363 (0)	...	...	...
...	...	1479 (2)	...	...	...	...
...	1581·1	1591 (2)	...	1583·6 (1)	1585·2	1583·4 (1)
1592 (1)	...		1588 (3)	...	...	...
	1604·9	1605 (2)	...	1604·1 (1)	1604·5	1607·4 (1)
	...	...	2946 (5)	2946·8 (2)	2946·9	2950·8 (2)
	...		...	3046·9 (1)	3045·4	3048·5 (1B)
3061 (10)	3056·4	3059 (3)	3058 (8)	3061·3 (4)	3060·1	3062·3 (4)
	...	...	...	3162·9 (1)	...	3160·5 (0)
	...	...	...	3184·8 (2)	3185·0	3184·0 (2)

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[4] Raman and Krishnan, Proc. Roy. Soc., 122, p. 23 (1929).

[5] Wood, Phil. Mag. VI, p. 729, (1928).

[6] Pringsheim and Rosen, Zs. f. Phy. 50, p. 741 (1928).

[7] Dadieu and Kohlrausch., Phys. Zs. 30, p. 384 (1929).

TABLE VI: Raman frequencies of chloroform.

Wood	Pringsheim and Rosen	Ganesan and[6] Venkateswaran	Langer and Meggers	Author.
262·1	257 (4)	261 (5)	261·1	262·3 (4)
365·5	368 (4)	367 (6)	365·8	366·9 (5)
668·2	666 (4)	669 (6)	668·4	667·2 (6)
757·1	766 (3)	762 (3)	760·1	761·8 (3B)
...	1214 (2)	1218 (2)	1215·0	1213·5 (2)
...	...	1441 (1)	...	1441·0 (1)
...	3009 (2)	3019 (4)	3018·7	3017·3 (2)
...	...	...	...	3072·4 (0*d*)

TABLE VII, Raman frequencies of carbon tetrachloride.

Raman and Krishnan	Wood	Pringsheim and Rosen	Ganesan and Venkateswaran	Langer and Meggers	Author.
219	216·3	217 (4)	216 (5)	218·8	217·7 (4)
312	313·0	315 (5)	313 (7)	313·9	315·6 (4)
457	456·9	458 (5)	459 (8)	459·3	459·7 (6)
768	757·1	757 (5)	762 (2)	758·1	759·9 (2*d*)
791	787·4	793 (5)	791 (2)	789·2	790·7 (2*d*)
...	...	1539 (2)	1535 (0)	1539·0	1535 (0d)

3. *Discussion of the Results.*

Benzene.—This liquid has been thoroughly studied by Söderqist and also by Langer and Meggers. The present investigation confirms the result of Söderqvist that the single band at 3μ found by earlier workers is in reality a group of five different bands of Raman-frequencies 3184·0 cm^{-1},

Ganesan and Venkateswaran—Ind. Journ. Phys. 4, p. 195 (1929).

3160·5 cm^{-1}. 3062·3 cm^{-1}. 3048·5 cm^{-1}. and 2950·8 cm^{-1}. The mean 3080 cm^{-1} of these five is in remarkable agreement with the infra-red frequency 3076 cm^{-1} of the single broad band at 3·25μ obtained by Coblentz. The frequency 3062·3 cm^{-1} is the most prominent one in this group, almost as intense as the 991·2 cm^{-1}. The corresponding Raman-lines are considerably broad, the estimated width of the 3048·5 cm^{-1} line is nearly 3 A.U, and that of the 3062·3 cm^{-1} line is 1·6 A. U. for λ4046 excitation.

The most prominent frequency is 991·2 cm^{-1}, the intensity and sharpness of the corresponding lines being comparable to some of the incident Hg lines. Other frequencies of benzene are weak except the 603·9 cm^{-1}.

In the present investigation two new feeble and diffuse lines with frequencies 22516·2 cm^{-1} and 22743·3 cm^{-1} are observed which have not been previously reported. The possible assignments of these lines are 422 cm^{-1} and 195 cm^{-1} due to λ 4358, or 2188 cm^{-1} and 1961 cm^{-1} due to λ4046. The former frequencies are too low to be admitted in the case of a compact molecule like benzene. The latter assignment appears to be more likely as the frequencies correspond to infra-red bands 4·6μ and 5·1μ which fall very nearly in the same position as some bands which Daugherty[9] gets in a recent infra-red study of benzene. No definite choice of the assignment can however be made until a single-line excitation picture is taken. Söderqvist also reported a feeble line 22792·7 cm^{-1} of uncertain assignment in this region.

One very interesting and remarkable thing that the author finds in the Raman spectrum of benzene is the presence of a winged nebulosity with fairly definite edges, accompanying the unmodified Hg lines. Similar nebulosities were observed by Raman and Krishnan, and Cabannes and Daure in their earliest studies. It has been explained as due to the

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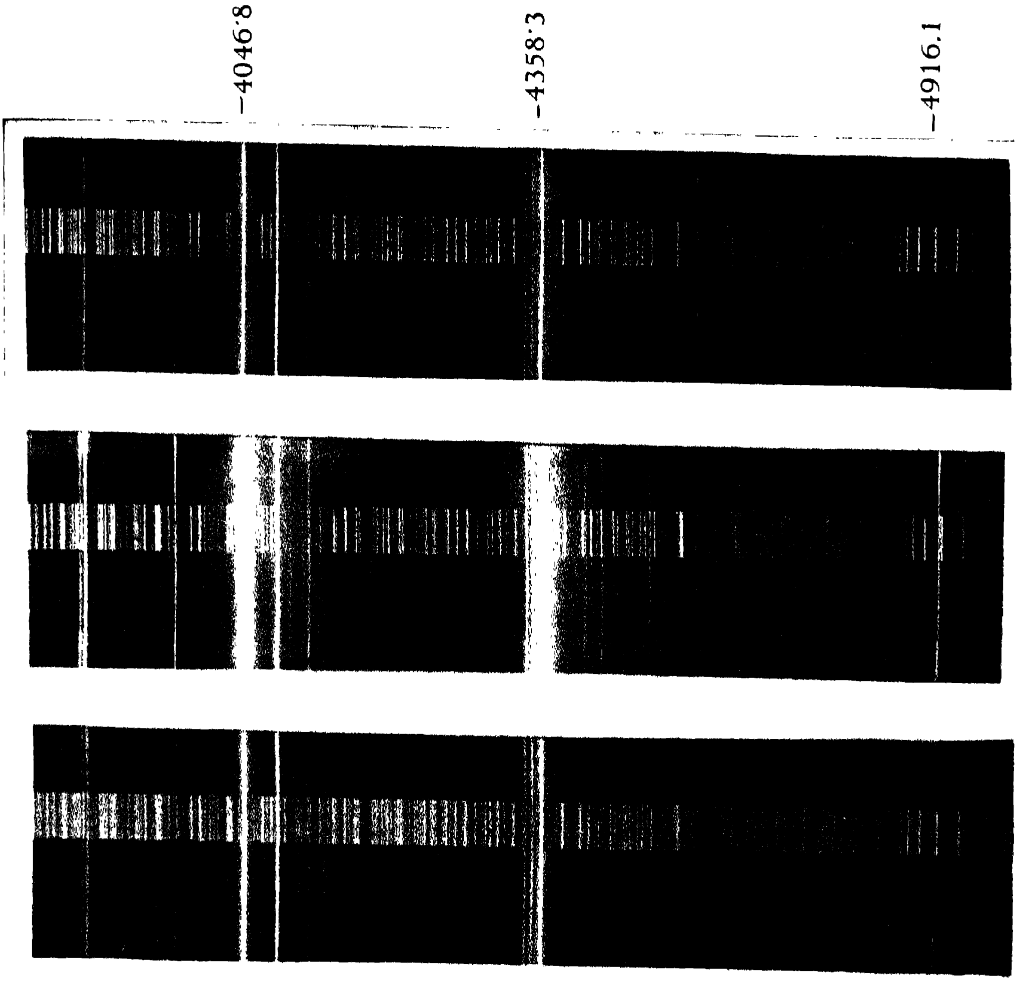
[9] Daugherty, Phy, Rev. 34, p.1549 (1929).



Raman Spectra

1. Benzene 2. Chloroform 3 Carbon tetrachloride

rotation of the molecules under the action of the incident light.[10] This nebulosity however does not show any structure under the fairly high dispersion employed in the present investigation. An interferometric study is in progress to study the nature of the origin of this nebulosity which is a general phenomenon observed in case of liquids with a fairly high degree of anisotropy.

Chloroform.—From table VI it will be seen that a new weak frequency 3072·4 cm^{-1} has been obtained for chloroform by the author. This shift is observed by three different excitations which gives this new frequency a definite footing. The band at 3μ is thus seen to be in reality a double one and not a single one as reported by Bhagavantam and Venkateswaran.[11] This band, assigned to the C—H vibrations is usually found to consist of a number of close components in case of aliphatic and also aromatic compounds, and it is not at all surprising that chloroform also shows the same splitting. In fact these two frequencies 3017·3 cm^{-1} and 3072·4 cm^{-1} are in close agreement with two frequencies 3022·1 cm^{-1} and 3071·5cm^{-1} which Rasetti [12] and others get in their study of the Raman spectrum of gaseous methane (the parent substance of chloroform). It is however very surprising that the most intense frequency 2914·8 cm^{-1} of methane is absent in chloroform.

A glance at the chloroform plate shows that each Raman line has a distinct character of its own, supporting the view that the observed Raman frequencies are none other than the fundamental frequencies of the chloroform molecule arising out of primary oscillations within the molecule. The three prominent frequencies 262·8 cm^{-1}, 367·5 cm^{-1} and 666·5 cm^{-1} give a first impression that they are all alike, but a careful examination of the lines shows that the first is distinctly the widest and the third decidedly the most intense and the sharpest.

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[10] Raman and Krishnan, Nature 122, pp. 278 and 882 (1928).

[11] Bhagavantam and Venkateswaran, Proc. Roy. Soc., p. 360 (1930).

[12] Dickinson, Dillon and Rasetti, Phy. Rev 34, p. 582 (1929).

Quite different in appearance from these three is the frequency 761·8 cm^{-1}, assigned to the C-Cl vibrations. The lines corresponding to this frequency have huge breadths, as much as 6 A. U. for the λ4358, 4 A. U. for the λ 4347 and 5 A. U. for the λ 4046 excitations. This breadth may be the result of the coupling of the rotation of the entire molecule with the C-Cl vibrations, superimposed on the small broadening due to the presence of the other isotope of chlorine.

Compared to the above the Raman lines corresponding to the frequencies 3017·3 cm^{-1} and 3072·4 cm^{-1} are much sharper. It may be noted here that the line corresponding to 3017·3 cm^{-1} due to λ4046 appears to be diffuse towards the red, the other lines show a slight shading towards the violet. As in benzene, the winged nebulosity makes its appearance here also, but it is very much narrower, as is expected due to its higher molecular weight and lower anisotropy.

Carbon tetrachloride.—Of the six observed frequencies the first three, *viz.*, 217·7 cm^{-1}, 315·6 cm^{-1} and 459·7 cm^{-1} can be placed in a distinctive group by themselves, the corresponding lines being intense and fairly sharp—although amongst themselves they differ from each other as regards their intensities and sharpness. The last one is the sharpest and the most intense, the other two being comparatively broader.

The lines corresponding to the doublet frequency 759·9 cm^{-1} and 790·7 cm are rather diffuse, but much sharper than the 761·8 cm^{-1} band of chloroform. There is a remarkable resemblance between these two lines as regards their intensity and diffuseness.

An important feature of all the Raman lines of this substance is that they are all slightly shaded off towards the violet, probably due to the presence of the chlorine isotope. The nebulosity observed in the previous two liquids has almost completely disappeared in this case. This gives a strong support to the view that this nebulosity is intimately connected with the molecular anisotropy.

4. *Conclusion.*

It will be seen from the above investigation that apart from accurate measurements, a high dispersion study of the Raman spectra helps to bring out valuable information as regards the spectral nature of the various Raman lines. Further work is in progress and will be communicated in due course of time.

In conclusion the author desires to express his sincere thanks to Professor Sir C. V. Raman for his inspiring guidance and interest in the progress of the work. The author is also thankful to the Nagpur University for the award of a Research Scholarship.

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Raman Spectra of the Mercaptans

BY

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ABSTRACT.

The paper describes the results of a study of the Raman spectra of methyl, ethyl, propyl, butyl, isobutyl, iso-amyl and phenyl mercaptans. A characteristic feature of the spectra of these compounds is the appearance of a prominent line at 2573. Hydrogen sulphide has been found by Bhagavantam to show this line in the same position and this frequency is therefore attributed to the SH oscillation. The prominence with which this frequency occurs in all the mercaptans is in marked contrast to the behaviour of the OH group which appears only in water and methyl alcohol but not in the higher alcohols. Two strong frequencies at about 659 and 739 also appear with all the mercaptans and are evidently due to the oscillation of the CS group. Differences in the nature of the oscillations between the CO and CS groups are pointed out. A definite decrease in the magnitude of the CS frequencies is noticed from methyl to ethyl mercaptan. In the higher members these frequencies attain a more or less steady value. The spectra of ethyl and the higher mercaptans show a number of very diffuse lines which are ascribable to the oscillations of the carbon chain. This character is presumably due to the influence of the sulphur atom on these oscillations.

A remarkable feature of the SH oscillation is that unlike the CH, NH and OH oscillations the value of this frequency does not change appreciably in any of its compounds. In like manner there is no large difference in the magnitude of the oscillation frequencies of C—S and C=S.

The data are compared with direct *infra-red* measurements made by Coblentz and Bell.

1. *Introduction.*

It is well known that from a study of the Raman spectra it is possible to identify certain oscillation frequencies with the presence of definite chemical linkages or groups. Several successful attempts have already been made in this direction. So far, however, no compounds containing SH groups have received any attention. In the present paper a study of the Raman spectra of some mercaptans has been made for the first time and the results of the investigation are reported.

2. *Experimental.*

With the exception of methyl mercaptan the liquids were all supplied by Messrs. Kahlbaum and were in all cases further purified by distillation in vacuum. Methyl mercaptan was prepared in the Palit Chemical laboratory by Mr. Adhikari and the liquid was purified by repeated distillation. The usual experimental arrangements were followed. The liquids were kept in Wood's tubes which were sealed off in vacuum. A two glass-prism spectrograph supplied by Adam Hilger giving a dispersion of about 20 A.U. per mm. at λ4000 was used for the experiments. The following tables show the analysis of the Raman lines. Under the columns I, ν, $\Delta\nu$, are given respectively, the intensities and the frequencies of the Raman lines and the differences in wave numbers between the exciting lines and the Raman lines. The incident lines λ3650·1, 3654·8, 3663·3, 4046·6, 4077·8, 4339·2, 4347·5 and 4358·3 are represented by the letters *a*, *b*, *c*, *d*, *c*, *f*, *g* and *h* respectively.

TABLE I.

Methyl mercaptan. CH_3SH.

I	ν	Δν	I	ν	Δν
5*d*	24814	*a*−2575	0	22291	*g*−704
2*d*	21779	*b*−2575	10	22235	*h*−703
3	24457	*a*−2932	10*d*	22133	*d*−2572 *h*−805
2	24422	*b*−2932	...	...	
0*d*	24381	*b*−2973	1*d*	21944	*e*−2572
1	24359	*c*−2931	1*b*	21880	*h*−1058
8	24001	*d*−704	1*b*	21833	*d*−2872
1*d*	23900	*d*−805	10*b*	21772	*d*−2933
1	23810	*c*−706	2*d*	21728	*d*−2977
0*d*	23713	*e*−803	0*d*	21646	*e*−2870
0	23646	*d*−1059	1*d*	21585	*e*−2931
0	23457	*e*−1059	0*d*	21513	*h*−1425

Δν :—704 (10), 805 (1d), 1059 (0), 1425 (0), 2573 (10), 2871 (0d), 2932 (10b) 2975 (2d).

TABLE II.

Ethyl mercaptan C_2H_5SH.

I	ν	Δν	I	ν	Δν
5*d*	24816	*a*−2573	10	22279	*h*−659
2*d*	24782	*b*−2572	0	22198	*h*−740
5	24456	*a*−2933	10 *d*	22132	*d*−2573
5	24422	{ *a*−2967	0	22065	*h*−873
		{ *b*−2932	1	21971	*h*−967
1	24388	*b*−2966	1	21943	*e*−2573
2	24357	*c*−2933	0 *b*	21885	*h*−1053
10 *dr*	24046	*d*−659	5 *b*	21830	*d*−2872
0 *d*	23967	*d*−738	10*b*	21772	*d*−2933
1	23858	*e*−658	6	21737	*d*−2968
			1*b*	21677	*h*−1261
1	23831	*d*−874	0	21641	*e*−2875
1	23741	*d*−964	1 *b*	21586	*e*−2930
1 *b*	23651	*d*−1054	2 *b*	21487	*h*−1451
0	23550	*c*−966	2	20064	*h*−2874
2 *b*	23440	*d*−1265	3	20008	*h*−2930
3 *b*	23258	*d*−1447			
2	22605	*h*−333			

Δν :—333 (2), 659 (10), 739 (0*d*), 874 (0), 965 (0), 1054 (1*b*), 1263 (1*b*), 1449 (3*b*), 2573 (10), 2872 (5*b*), 2933 (10*b*), 2968 (7*b*).

TABLE III.

Propyl mercaptan $CH_3.CH_2.CH_2.SH$.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
4 *b*	24814	*a*−2575	3	22571	*h*−367
1	24778	*b*−2576	4	22286	*h*−652
4 *b*	24455	*a*−2934	1*d*	22234	*h*−694
5 *b*	24423	*a*−2969	1*d*	22208	*h*−730
		b−2929	8*b*	22130	*d*−2575
		c−2865	0	22054	*h*−884
2	24384	*b*−2970	0	21974	*h*−964
2	24359	*c*−2931	2*b*	21904	*d*−1034
3 *b*	24052	*d*−653	4 *b**	21831	*d*−2874
0 *d*	24008	*d*−697	8*b**	21779	*d*−2926
0 *d*	23976	*d*−729	5*b*	21739	*d*−2966
0	23864	*c*−652	0	21694	*g*−1301
0	23823	*d*−882	1	21638	*h*−1300
0	23741	*d*−964	1	21582	*e*−2934
1 *b*	23673	*d*−1032	0	21552	*g*−1443
0 *b*	23482	*e*−1034	2*d*	21494	*h*−1444
0 *b*	23407	*d*−1298	2*b*	20066	*h*−2872
1	23266	*d*—1439	3*b*	20011	*h*−2927
			2	19972	*h*−2966

$\Delta\nu$:—367 (3), 652 (4), 695 (1*d*), 730 (1*d*), 883 (0), 964 (0), 1033 (2*b*), 1299 (1*b*), 1441 (2*b*), 2575 (8*d*), 2874 (4*b*), 2930 (8*b*), 2966 (5*b*).

* Each of these lines appears to be accompanied by a component, but owing to want of proper resolution exact measurements could not be made.

TABLE IV.

Butyl mercaptan $CH_3.CH_2.CH_2.CH_2.SH$

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
4*d*	24816	*a*−2573	0	22501	*h*−437
1	24780	*b*−2574	0	22340	*g*−655
1	24480	*b*−2874	6	22282	*h*−656
3	24456	*a*−2933	0*b*	22231	*h*−707
3	24422	*a*−2967	10*d*	22131	*d*−2574
0	24395	*b*−2959	0	22096	*h*−842
0	24354	*c*−2936	0*b*	22049	*h*−889
0	24269	*d*−436	1	21983	*h*−955
5	24048	*d*−657	1	21941	*e*−2575
0*b*	23997	*d*−708	1*b*	21890	*h*−1048
1*b*	23860	*c*−656	8*b*	21836	*d*−2869
		d−845	7*b*	21779	*d*−2906
1*b*	23820	*d*−889	10*b*	21771	*d*−2934
0	23758	*d*−947	6*b*	21741	*d*−2964
1*b*	23655	*d*−1050	2*b*	21644	*h*−1294
0	23599	*d*−1106	1*b*	21576	*e*−2940
2*b*	23408	*d*−1297			*h*−1362
0*b*	23346	*d*−1359	0*b*	21555	*e*−2961
3*b*	23271	*h*−1434	3*b*	21495	*h*−1443
1	22640	*d*−298	2	20069	*h*−2869
2	22605	*h*−333	2	20033	*h*−2905
			2	20004	*h*−2934

$\Delta\nu$:—298 (1), 333 (2), 437 (0), 656 (6), 707 (0*b*), 843 (0), 889 (0*b*), 951 (1) 1049 (1*b*), 1106 (0), 1296 (2*b*), 1361 (0*b*), 1438 (3*b*), 2574 (10*d*), 2869 (8*b*), 2905 (7*b*), 2934 (10*b*), 2964 (6b).

TABLE V.

Isobutyl mercaptan, $(CH_3)_2CH.CH_2SH$.

I	ν	Δν	I	ν	Δν
5*d*	24814	*a*−2575	2	22510	*h*−428
2*d*	24780	*b*−2574	0	22416	*h*−522
3*b*	24473	*a*−2916	3	22267	*h*−671
6*b*	24428	*a*−2961	5*dr*	22231	*h*−707
		b−2926	1*d*	22169	*h*−769
3*b*	24395	*b*−2959	10*d*	22127	*d*−2578
3*b*	24369	*c*−2921	0*b*	22098	*h*−840
		d−336	1*b*	22010	*h*−928
2	24277	*d*−428	3*d*	21982	*h*−956
0	24089	*e*−429	1	21942	*e*−2574
1	24036	*d*−669	0	21868	*h*−1070
3*dr*	23997	*d*−708	10*b**	21833	*d*−2872
1*d*	23934	*d*−771	8*b**	21780	*d*−2925
0*d*	23877	*d*−828	10*b*	21733	*d*−2972
1*d*	23787	*d*−918	0	21689	*h*−1249
2*d*	23750	*d*−955	2*b*	21629	*h*−1309
0*b*	23488	*d*−1217	……	……	*e*−2887
0*b*	23452	*d*−1253	2*b*	21545	*e*−2971
2*b*	23378	*d*−1327	3*b*	21511	*h*−1427
2*b*	23284	*d*−1421	3*b*	21480	*h*−1458
3*b*	23243	*d*−1462	3	20071	*h*−2867
0	22705	*h*−233	2	20018	*h*−2920
3	22599	*h*−339	3	19982	*h*−2956
0	22534	*h*−404	…	……	……

Δν :—233 (0), 338(3), 404(0), 428(2), 522(0), 670(3), 707(5*dr*), 770(1*d*), 834(0*b*), 923(1*b*), 956(3*d*), 1070(0), 1217(0*b*), 1251(0*b*), 1327(2*b*), 1424(3*b*), 1460(3*b*), 2575(10*d*), 2870(10*b*), 2925(8*b*), 2966(10*b*).

* These lines appear to have components but owing to want of proper resolution exact measurements could not be made.

TABLE VI.

Isoamyl mercaptan, $(CH_3)_2CHCH_2SH$.

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
5*d*	24815	$a-2574$	3	22514	$h-424$
2	24777	$b-2577$	5	22276	$h-662$
2	24456	$a-2933$	2*d*	22223	$h-715$
8	24426	$a-2963$	2*dr*	22197	$h-741$
...	......	$b-2928$	10*d*	22127	$d-2578$
...	......	$d-279$	...	......	$h-811$
2	24392	$b-2962$	0	22081	$h-857$
1	24354	$c-2935$	0	22009	$h-929$
1	24286	$d-419$	2	21983	$h-955$
4	24049	$d-656$	2	21942	$e-2574$
0*b*	23983	$d-722$	0*b*	21899	$h-1039$
1*dr*	23964	$d-741$	10*b**	21836	$d-2869$
1*b*	23887	$d-818$	7*b**	21773	$d-2932$
1*b*	23852	$d-853$	10*b**	21743	$d-2962$
...	......	$e-664$	0*b*	21698	$g-1297$
0*b*	23668	$d-1037$	5*b*	21641	$h-1297$
0*b*	23591	$d-1114$	...	......	$c-2875$
0*dr*	23520	$d-1185$	5*b*	21592	$h-1346$
1	23418	$d-1287$	...	......	$e-2924$
1	23405	$d-1300$	4*b*	21555	$e-2961$
1*dr*	23377	$d-1328$	6*dv*	21467	$h-1471$
4*dv*	23237	$d-1468$	5	20067	$h-2871$
0	23220	$h+282$	...	......	$g-2928$
5	22659	$h-279$	3	20014	$h-2924$
0	22556	$g-429$ *	5	19976	$h-2962$

$\Delta\nu$:—279(5), 422(3*b*), 659(5), 719(2*d*), 741(2*dr*), 818(1*b*), 855(0), 929(0), 955(1), 1038(0*b*), 1114(0*b*), 1185(0*b*), 1287(1), 1300(1), 1337(2*dr*), 1470(6*dv*), 2574(10*d*), 2870(10*b*), 2929(7*b*), 2962(10*b*).

* All these lines appear to have a structure but as they are not properly resolved exact measurements could not be made.

TABLE VII.

Phenyl mercaptan, C_6H_5

I	ν	$\Delta\nu$	I	ν	$\Delta\nu$
0	24425	*d*−280	5*d*	22744	*h*−194
2*b*	24324	*a*−3065	2*d*	22656	*h*−282
...	......	*e*−192	3	22523	*h*−415
2	24290	*d*−415	0	22419	f−620
...	......	*b*−3064	0	22375	*g*−620
2	24235	*c*−3055	0	22339	*h*−599
...	......	*e*−281	3	22319	*h*−619
0	24113	*d*−592	3	22243	*h*−695
2	24090	*d*−615	0*b*	22216	*h*−722
2	24010	*d*−695	7*d*	22136	*d*−2569
0*b*	23967	*d*−738	4*dv*	22020	*h*−918
0	23820	*e*−696	0	21991	*g*−1004
2*d*	23786	*d*−919	...	......	......
...	......	......	10	21938	*h*−1000
10s	23705	*d*−1000	...	......	*e*−2578
4s	23680	*d*−1025	4	21915	*h*−1023
0	23637	*d*−1068	0	21865	*h*−1073
3	23618	*d*−1092	3	21845	*h*−1093
3	23587	*d*−1118	3	21819	*h*−1119
2	23551	*d*−1154	2	21779	*h*−1159
...	......	......	1*b*	21760	*d*−2945
2	23516	*e*−1000	8*dv*	21646	*d*−3054
0	23429	*e*−1087	1*d*	21567	*h*−1371
0	23402	*c*−1114	0*d*	21508	*h*−1430
0*b*	23347	*d*−1351	2	21462	*c*−3054
0*b*	23271	*d*−1434	0*b*	21415	*g*−1580
0*b*	23203	*d*−1502	...	......	*h*−1523
7	23123	*d*−1582	5	21352	*h*−1586

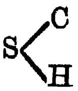
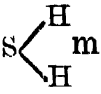
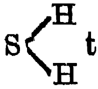
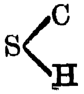
$\Delta\nu$:—194(5*d*), 282(2*d*), 415(3), 596(0), 618(3), 695(3), 730(0*b*), 918(4*d*), 1000(10), 1024(4), 1071(0), 1092(3), 1118(3), 1157(2), 1361(1*d*), 1432(0*d*), 1502(0*b*), 1584(5), 2573(7*d*), 2945(1*b*), 3059(8*d*).

3. *Discussion of Results.*

In the following table are given the Raman frequencies which are common to all the aliphatic mercaptans investigated in this paper. The figures in the brackets indicate their intensities.

Table VIII.

Substance.	Δν.			
Methyl mercaptan ...	704 (10)	805 (1)	1059 (0)	2573 (10)
Ethyl ,, ...	659 (10)	739 (0)	1054 (1)	2573 (10)
Propyl ,, ...	652 (4)	730 (1)	1033 (2)	2575 (8)
Butyl ,, ...	656 (6)	707 (0)	1049 (1)	2574 (10)
Isobutyl, ,, ...	670 (3)	770 (1)	1070 (0)	2575 (10)
Isoamyl ,, ...	659 (5)	741 (2)	1038 (0)	2574 (10)

It will be seen that there are four frequencies 704, 805, 1059 and 2573 which persist throughout the group. Evidently they all arise from a common configuration  $S\begin{smallmatrix}C\\H\end{smallmatrix}$ present in them.[1] On the view that Δν 600 and 800 represent only one oscillation, (this point will be dealt with more fully in a later section), the total number of vibrational frequencies, namely, three, suggests clearly that the three atoms are arranged in the form of a bent model. In this connection we may mention that  $S\begin{smallmatrix}H\\H\end{smallmatrix}$ molecule is known to be highly polar[2] which indicates that this molecule has a triangular arrangement. Since the mercaptans may be considered as derivatives of  $\mathrm{S}{<}^{\mathrm{H}}_{\mathrm{H}}$ this offers a further support to the above view regarding the arrangement of the configuration  $\mathrm{S}{<}^{\mathrm{C}}_{\mathrm{H}}$. However, as we do not know the nature of the forces or the inclination of the bonds a precise theoretical treatment is not possible.

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[1] Similar discussions have been given by Venkateswaran and Bhagavantam in a previous paper on alcohols in the same volume.

[2] See P. Debye "Polar Molecules," p. 40 (1929).

A consideration of methyl mercaptan, which is the simplest of the compounds investigated, throws however, some light on the nature of these oscillations. The spectrum of this compound is comparatively simple and shows Raman lines corresponding to $\Delta\nu$ 704, 805, 1059, 1425 2573, 2871, 2932 and 2975 (See Table I). Of these, the lines at 1425, 2871, 2932 and 2975 may be definitely attributed to the presence of the CH group. Of the remaining frequencies $\Delta\nu$2573 is the most important as it appears prominently in all the mercaptans and is not found in any other class of compounds investigated so far. Liquid hydrogen sulphide which has recently been investigated in this laboratory by Bhagavantam also shows this line prominently in the same position. One may therefore conclude that this frequency (2573) is characteristic of the SH group present in these compounds.

It is of interest to compare here the SH oscillation frequency with those characteristic of the CH, OH and NH groups. In conformity with the fact that hydrogen which is involved in these oscillations is the lightest atom all these frequencies are high. All of them give rise to broad bands. The case of CH group is particularly interesting as the band consists of various components ranging from 2800 to 3320. All these oscillation frequencies differ, however, entirely from that due to the SH group in one important aspect. While considerable variations are observed in the magnitude of the CH, OH, and NH oscillations as we pass from the simplest to the more complex compounds containing these groups, there is no change at all in the value of the SH frequency in hydrogen sulphide and in the various aliphatic and aromatic mercaptans. Such a remarkable constancy (See Table VII) in the SH frequency is of fundamental significance. This difference in the nature of the SH oscillation as contrasted with the other oscillation frequencies mentioned above implies an essential difference in the manner of combination of the sulphur atom on the one hand and the group of carbon, oxygen and nitrogen atoms on the other. In addition to this it is also to be remembered that the sulphur atom is comparatively heavy and hence less liable to be influenced by the neighbouring groups.

In this connection it is interesting to compare the behaviour of the OH and SH oscillations in the early members. In water the presence of the OH group gives rise to a broad band at 3400 which is less intense and sharper in methyl alcohol and does not appear in the higher alcohols. Quite unlike this, the Raman frequency characteristic of the SH group which is prominent and sharp in hydrogen sulphide continues to appear with more or less the same intensity in methyl mercaptan and the higher members of the series, but is distinctly more diffuse.

The value of the frequency characteristic of the SH group may be calculated from the masses of these atoms and the strength of binding on the basis of the formula $\nu=k\sqrt{\frac{A}{\mu}}$. Taking the thermochemical dissociation constant between sulphur and hydrogen as 75 K cal. per Mol. we get the value 2486 as compared with the observed value 2573.

Next in importance are the ones at $\Delta\nu$704 and 805. These frequencies appear although slightly shifted in position in all the mercaptans and evidently owe their origin to the presence of the SC group. Of the two $\Delta\nu$704 is very intense and fairly sharp while Δν 805 is comparatively less intense and much more diffuse. The values of these frequencies fall down to 659 and 739 in ethyl and 652 and 730 in propyl mercaptans, thus assuming more or less steady values in the higher members. Such a shift of these oscillations towards the longer wave length is very significant in that it indicates the influence of the heavier groups on them.

The appearance of such an additional and less prominent frequency characteristic of the CS oscillation is not easily understood. In this connection we may refer to the case of carbon disulphide. Here also we get two frequencies at 655 and 800, the first one being much sharper and more intense than the other. In view of the nonpolar nature of this liquid and the now accepted linear model for this molecule it is difficult to reconcile the appearance of these two frequencies so close together in the spectrum of CS_2. Carbon dioxide which is also nonpolar and has a linear model presents similar difficulties. In a recent paper Bhagavantam[1] has discussed this question and has shown from polarisation measurements that all these Raman lines represent in reality only variants of one symmetrical or inactive oscillation. Similar conclusions have also been recently arrived at by Snow[2] for CO_2 and CS_2. It is therefore not surprising that in the mercaptans we have a similar phenomenon and that the characteristic oscillation of the SC group consists of two frequencies, one of them being the principal one and the other subsidiary.

Another important feature of the oscillations due to the SC group may be noted here. In the mercaptans the sulphur and carbon atoms are attached with a single bond, whereas in carbon-disulphide they are obviously attached with a double bond. One should therefore expect that the characteristic oscillations due to these two different kinds of bindings would be widely different. In fact, changes in the nature of the linkage between a carbon atom and a carbon or other atom such as C – C, C = C, or C—C, and C—O or C = O etc. are known to produce large variations in the magnitude of the characteristic frequencies according as the bond between them is single, double or triple. Surprisingly, however, in the case of the oscillations of the SC group the nature of the linkage between the two atoms does not appear to influence to any great extent the magnitude of these frequencies. In other words, the chemical difference between the S—C and S = C groups is not accompanied by any appreciable difference in the oscillation frequencies of the two groups. We may here refer to the results obtained by Pal and Sen Gupta[1] who find that the frequency 756 which is presumably due to C = S bond in phenyl mustard oil does not differ appreciably from that of C—S bond in thiocyanates, namely, 741.

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[1] S. Bhagavantam :, Ind. J. Phys., Vol. V, p. 59, 1930.

[2] C. P. Snow, Proc. Roy. Soc., Vol. 128, p. 294, 1930.

Coming to the other aliphatic mercaptans we find that in addition to the lines present in methyl mercaptan several new lines appear in the spectra of the higher members. In addition to the lines which may be attributed to the characteristic oscillation frequencies of the SH, CH and SC groups the spectra show a number of broad bands many of them being 5 to 8 A. U. wide. All these oscillations are ascribable to the carbon chain. The unusual width and diffuseness of these lines in the mercaptans as contrasted with similar C – C oscillations in the corresponding alcohols and hydrocarbons may presumably be referable to the influence of sulphur atom on these oscillations.

Of the oscillations common to the mercaptans it should be remarked that unlike the CS frequencies the change in the magnitude of $\Delta\nu$ 1059 is very small from methyl to ethyl mercaptans.

Of the many smaller frequencies which occur in the higher mercaptans the one at 332 is of interest. This is absent in methyl mercaptan but appears with large intensity in the other compounds. It shows some variations in its magnitude in the compounds investigated.

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[1] N. N. Pal and Sen Gupta, Ind. J. Phy., Vol. V, p. 13, 1930.

A remark regarding the difference in behaviour of the C—S and the analogous C—O oscillations may be made here. While the latter oscillation with a frequency of 1050 wave numbers appears strongly in methyl alcohol, but only very weakly in the higher alcohols the C—S oscillation continues to appear prominently in all the mercaptans.

The character of the CH band[1] in the various hydrocarbons has already been discussed in a previous paper. One observation regarding the relative intensities of the components of this band may be noted. The central component of this band is the most intense in methyl, ethyl and propyl, but is the weakest in isobutyl and isoamyl mercaptans. This feature appears to be of a general nature as a comparison of the CH band in other organic compounds also shows that the central component is usually the most intense in the normal compounds, but is the weakest in the isomers.

It may be mentioned that some of the components of the CH band with the liquids recorded in this paper were rather broad and apparently capable of further resolution. Under suitable conditions a doublet structure in some of them could be seen although exact measurements were not possible. Especially is this the case with propyl and the higher mercaptans.

Phenyl mercaptan is the only aromatic compound investigated in this paper and a few remarks may be made regarding its spectrum. The liquid shows strong absorption in the ultra-violet region beyond λ4046. The most prominent frequency is the one at 1000, the CH and SH frequencies coming next in order of intensity. The two frequencies at 2945 and 3059 of which the latter is more intense are both attributable to the CH group. A striking feature of the spectrum of this liquid is the presence in it of a number of doublets. Practically every benzene line is accompanied by a more or less bright line on the longer wave length side. The significance of such a splitting in benzene derivatives and its relation to a similar phenomenon in the electronic band spectra of these molecules have been pointed out in a recent paper by Venkateswaran and Bhagavantam.[1] In conformity with the observations made in this paper we find in phenyl mercaptan the appearance of a prominent new frequency at 1024 and the shifting of the 992 benzene frequency to 1000.

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[1] S. Venkateswaran and S. Bhagavantam, Ind. J. Phys., Vol. V, p. 129, 1930.

The spectrum of phenyl mercaptan shows several fairly intense small frequency shifts at 194, 282, and 415, of which the one at 194 is strikingly prominent. The appearance of such small frequency shifts may be understood when we remember that the benzene ring is subjected to a great strain owing to the loading of one end with a heavy sulphur atom.

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[1] S. Venkateswaran and S. Bhagavantam, Proc. Roy Soc., Vol. 128, p. 252, 1930.

TABLE IX.

Ethyl mercaptan		Propyl mercaptan		Butyl mercaptan		Isoamyl mercaptan.	
λ Ra	λ i.r.	λ Ra	λ i.r.	λ Ra	λ i.r.	λ Ra	λ i.r.
30·0(2)		27·2(3)		33·6(4)		35·8(5)	
				30·0(0)			
				22·9(0)		23·7(3)	
15·17(10)		15·34(4)		15·24(6)		15·17(5)	
		14·39(1)		14·14(0)			
						13·91(2)	
13·53(0)		13·70(1)				13·50(4)	
	12·65(*m*)						
						12·22(1)	
			11·8(*w*)	11·86(0)	11·9(*w*)		11·9(*w*)
11·44(0)	11·6(*s*)	11·33(0)	11·4(*w*)	11·25(0)	11·4(*w*)	11·66(0)	11·5(*w*)
			10·8(*w*)			10·76(1)	10·8(*m*)
10·36(0)	10·34(*s*)	10·37(0)		10·52(1)	10·4(*m*)	10·47(1)	
							10·1(*w*)
9·49(1)		9·68(2)	9·8(*w*)	9·53(1)	9·7(*w*)	9·63(0)	9·8(*w*)
	9·25(*s*)				9·4(*w*)		9·4(*s*)
			8·9(*s*)	9·04(0)	9·0(*s*)	8·98(1)	9·0(*m*)
						8·44(1)	8·6(*w*)
7·92(1)	8·05(*s*)	7·70(1)	7·9(*s*)		8·0(*s*)	7·77(1)	8·0(*s*)
			7·6(*s*)	7·72(2)	7·7(*s*)	7·69(1)	7·7(*s*)
			7·2(*m*)	7·35(0)	7·3(*m*)	7·48(2)	7·2(*s*)
	7·2(*s*)						
6·90(3)	7·1(*s*)	6·94(2)	6·8(*s*)	6·95(3)	6·8(*s*)	6·80(6)	6·8(*s*)
	5·8(*m*)						6·4(*s*)
							6·0(*s*)
			4·9(*w*)		4·8(*w*)		5·0(*s*)
			4·6(*w*)		4·4(*w*)		4·1(*w*)
3·887(4)	4·0(*s*)	3·883(8)	3·8(*s*)	3·885(10)	3·8(*s*)	3·885(10)	3·8(*s*)
3·482(5)		3·479(4)		3·486(8)		3·484(10)	
3·409(10)	3·45(*s*)	3·413(8)		3·412(7)		3·414(7)	
				3·408(10)			
3·369(7)		3·372(5)	3·3(*s*)	3·374(6)	3·3(*s*)	3·372(10)	3·3(*s*)

The infra-red absorption spectra of ethyl, n-propyl and isoamyl mercaptans in the region 1 to 12 μ have been investigated, the first by Coblentz[1] and the other two by Bell.[2] The values obtained by them are tabulated for comparison with those shown by the Raman spectra (see Table VIII). The intensities of the infra-red absorption bands are represented by the letters *s*, *m*, and *w* indicating strong, medium and weak respectively. It will be seen that there is a fair agreement between the two sets of values. The value of the SH band obtained by Bell from infra-red absorption varies from 3·85 μ to 3·90 μ which is in good agreement with the value 3·88μ shown by the Raman spectra. The value obtained by Coblentz for this band in ethyl mercaptan is somewhat large. It may be mentioned, however, that according to Coblentz the value obtained by Julius with this liquid is 3·88 μ which agrees surprisingly well with 3·883 μ shown by the Raman spectrum. The absorption spectra of some mercaptans in the near infra-red region have been investigated by Ellis[3] who finds a band at 1·99 μ to 2·0μ characteristic of this class of compounds. He suggests that the 3·9μ and 2·0μ bands are probably the fundamental and the first overtone bands associated with the SH linkage.

The author desires to exprcss his best thanks to Prof. Sir C. V. Raman, F.R.S. for his constant encouragement and interest in the work and to Prof. Sir P. C. Ray for his great kindness in loaning the chemicals which made this investigation possible.

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[1] W. W. Coblentz, "Investigations of Infra-red Spectra," Vol. I, Carnegie Institution. 1905.

[2] F. K. Bell, Berichte, 60 B, p. 1749, 1927.

Bell's values (unpublished) quoted by J. W. Ellis (J. Amer. Chem. Soc. Vol. I, p. 2116, 1929.

[3] J. W. Ellis, *loc. cit.*

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18

The Raman Effect.

Its Significance for Physics and Chemistry.

By

S. BHAGAVANTAM.

1. *Introduction.*

It is very generally recognised that the optical effect discovered by Sir C. V. Raman besides being a phenomenon of great theoretical interest has opened a new chapter in spectroscopy and furnished physicists and chemists with a convenient and fruitful method of research into problems concerning the structure of matter. The study of the effect has, in consequence, attracted investigators of eminence and gained adherents in numerous centres of research. The literature of the subject has grown rapidly, and in lieu of the 160 papers abstracted a year ago by Dr. Ganesan in a special number of the Indian Journal of Physics, we have at the present time some 350 references making up the bibliography of the Raman effect. In an appendix to this essay, the author has collected these references together and classified them under suitable subject-headings. An index of authors and an alphabetical list of the substances studied by them have been appended to the bibliography. It is hoped that these may prove useful to those actively interested in the subject and that the indexes provided may enable references to be readily traced to the work of individual authors or to information concerning particular substances.

In view of the rapid growth of the subject and the interest attaching to it, the author has thought it desirable to offer a brief survey of its development and especially of the different ways in which the Raman effect has proved to be of significance for physics and chemistry.

2. *Relation to Earlier Work.*

It seems proper to emphasise that though the existence of the Raman effect may be regarded as a vindication of the quantum theory of radiation and of the new mechanics, its discovery was independent and resulted from the experimental work on the scattering of light carried on continuously at Calcutta since the year 1921. In an essay published by the Calcutta University in February, 1922, Prof. Raman outlined his programme of research which included a comprehensive study of the scattering of light in numerous substances over the widest range of physical states and conditions, and, a comparison of the results obtained with the consequences of existing theories; it was confidently anticipated that the results would throw light on fundamental questions concerning the structure of molecules, molecular aggregation in solids and liquids, and upon the nature of radiation itself. The programme thus outlined was systematically pursued, and nearly 100 communications emerged from the laboratory during the six years following the publication of the essay. They dealt with the subject in all its varied aspects and relations to other fields of research. It was natural that the investigations should have revealed at a very early stage the existence, in association with the Rayleigh-Einstein type of scattering, of secondary radiations of altered wave-length. In his lecture on a "New Radiation," Prof. Raman has referred to observations made and published as early as 1923 which unmistakably showed the existence of such radiations. He has also described how he was led to the recognition of the universality of this phenomenon, to the observation that such secondary radiations were often strongly polarised (thus sharing the character of the scattered rays), and to the discovery of their spectral character under monochromatic excitation and finally of their relation to the frequency of the exciting radiation and the chemical nature of the substance studied.

In view of the importance of the earlier investigations to students of light-scattering, the author has collected references to the literature on the subject published from Calcutta and appended it to this essay.

3. *Nature of the Effect.*

Reference has already been made to the universality of the new type of light-scattering. The fact that it may be observed in a great variety of substances and in diverse physical states or conditions, and that the results are different in each different case makes the field of investigation very extensive and brings it into relationship with many other branches of physical and chemical research. As actually observed, the effect consists in the appearance of new lines (or in some cases bands) and generally also some unresolved continuous radiation in the spectrum of the scattered light, besides the lines originally present in the incident radiation. Each line in the incident spectrum, if of sufficient intensity, gives rise to its own set of lines or bands and associated continuous spectrum; the frequency shifts are independent of the incident radiation and are therefore characteristic of the particular material studied.

In the scattering of light with altered frequencies, we are evidently dealing with a case in which there is an exchange of energy between the quantum of radiation and the scattering medium according to the scheme—$\text{Molecule} + h\nu \rightleftarrows \text{Molecule}^* + h\nu$.* In the case of free molecules scattering light, we can obviously distinguish between three different kinds of effect, an electronic effect, a rotational effect and a vibrational effect, the classification indicating the particular type of energy in the molecule which is added to or given up. Most of the observed Raman lines with moderate or large frequency shifts have evidently to be interpreted as due to a vibrational effect. Except in the case of molecules with very small moment of inertia, lines due to the rotational effect would correspond to rather small frequency shifts and appear close to the incident lines and might even fail to be resolved from them and from each other.

It is noteworthy that the Raman lines generally show great differences in their intensity and in their width, some being sharp and others diffuse or even broad bands. It is an important property of the Raman radiations observed in the transversely scattered light that they are often strongly polarised. The extent of such polarisation however varies enormously for radiations of different frequency shifts, and this is a very significant point to be considered in relation to their origin.

The continuous spectrum also shows great variations in intensity with different materials. It generally appears as wings extending unsymmetrically on either side of the principal (incident) lines and shows little or no polarisation : in this case it is most probably an unresolved rotational effect. A continuous spectrum, having possibly a different origin, appears with very viscous liquids and may be so strong as to overpower all the other lines. Some impure liquids also exhibit a general or continuous radiation in their Raman spectrum : a similar effect develops progressively in liquids that undergo chemical change under the action of light.

4. *Its Significance as a Radiation Effect.*

Quite apart from its various useful applications in physics and chemistry, the Raman effect possesses a unique interest with reference to the problem of the nature of radiation, the interaction of matter with radiation, and optical theories generally. In the Compton effect we have the case of an electron weakly bound to an atomic nucleus acquiring momentum and being freed from the atom as the result of its scattering a quantum of radiation; the nucleus plays a minor part in the process. In the Raman effect, on the other hand, we are dealing with the most general case of interaction between the quantum of radiation and matter; the latter may be the molecule of a gas or even a molecular aggregate such as a liquid or a crystal. The relationship between the two effects becomes clearer if we limit ourselves to a case in which the scattering particle is a single molecule which undergoes only a change in its electronic energy. We then have an electronic Raman effect, which becomes identical with the Compton effect if the electron is actually dislodged and rendered free, but differs from it if the electron remains bound to the molecule in a higher level of energy.

Prima facie, the exchange of energy between the molecule and the quantum may be in either direction indifferently. In other words, we may have in the Raman effect, also an increase of frequency in scattering and not merely a decrease of frequency as in the Compton effect. As is well-known, this was fully substantiated by the investigations of Raman and Krishnan who showed further that the ratio of the intensities of the radiations of diminished and increased frequencies was the same as the ratio of the populations of normal and thermally excited molecules giving rise to them as found from the Boltzmann theorem. This may justly be regarded as a beautiful proof, not only of the real existence of discrete stationary states, but also of the perfect reversibility of the interaction between radiation and matter, and an experimental proof that the Boltzmann formula correctly gives the proportionate number of thermally excited molecules. As an illustration of the general principle, we may mention the case of diamond in which the present writer has found that corresponding to the principal Raman line whose frequency is less by 1332 wave-numbers than that of the incident radiation, there is also a line whose frequency is greater by the same amount, but whose intensity is only about a thousandth part of the other.

It is not necessary here to enlarge further on the relation between Raman effect and the theory of optical dispersion as developed by Kramers and Heisenberg. It is well known that the latter has been the starting point for the development of the new mechanics.

5. *Its Significance to Spectroscopy.*

The Raman effect has made available for the study of molecular spectra in the infra-red the most convenient and precise of all physical methods, namely, the photographic measurement of spectra. The improvements in technique during the last two years have made it possible to photograph the effect with instruments of reasonably large dispersion and thereby with success to aim at high accuracy of measurement. Thus by working in the visual or ultra-violet region of the spectrum we obtain with equal facility, precise measurements of characteristic frequencies of molecules or of molecular aggregates lying both in the near and in the remote infra-red region and corresponding to wave-lengths lying between, say, 3μ and 200μ. Considering the laborious and difficult nature of the work in the infra-red region, especially for wave-lengths greater than 15μ, and the precision attained, this is obviously an immense gain. Further, the nature of the information obtained is different from that given by the infra-red spectroscope. With the latter we obtain a complex of bands due to the superposition of vibration and rotation, and complicated by the occurrence of overtones and combinations of the fundamental frequencies. In the Raman effect, on the other hand, there is clear evidence that the vibrational frequencies obtained are the fundamentals only, overtones and combinations not usually being observable. Thus the results obtained from the Raman effect help to clarify and elucidate the results given by infra-red spectroscopy. A beautiful illustration of this is the recent work of Krishnamurti at Calcutta with crystalline rhombic sulphur. He has shown that the fundamental frequencies of this substance lie in the remote infra-red between 20μ and 120μ, and all the near infra-red absorption bands are merely overtones or combinations. Numerous examples of this kind may be quoted in the case of other substances and especially of organic compounds, as for instance the case of carbon tetrachloride which has been recently discussed very carefully by Prof. Clemens Schaefer.

A very interesting relationship between the Raman effect and infra-red spectroscopic data is that in the former we often find coming out in great strength just those frequencies which fail to appear in infra-red absorption. This may be due to the symmetric oscillations having no electric moment and therefore inactive as in the cases of CO_2, CS_2, NO_3^-, CO_3^{--} etc., or due to the selection rules for the Raman effect and infra-red absorption being quite different. As an illustration of the latter, the case may be cited of HCl which, as found by R. W. Wood, shows the missing Q branch in its Raman spectrum.

The electronic band spectra of diatomic molecules have been extensively studied of recent years and great progress has been made in their theoretical interpretation. In the case of those diatomic gases for which we have Raman effect data, a correlation has been successfully established between the vibrational and rotational frequencies as determined from it and from the band spectrum results. The brilliant work of R. W. Wood, McLennan and Rasetti in this connection is very well known. The present writer has succeeded in photographing the Raman effect with liquid chlorine and the vibrational frequency found agrees very well with the band spectrum value.

When we pass from diatomic to polyatomic molecules, we enter a region of great complexity, in the elucidation of which Prof. Henri and his collaborators at Zurich have been pioneers. Prof. Henri has found that the Raman spectra of the substances studied by himself and his students furnish the key to the analysis of their absorption and fluorescence spectra as observed in the visible and ultra-violet regions. The bands observed in such spectra are very numerous and a knowledge of the vibrational frequencies of the molecules enables the process of arranging them and interpreting their origin to be undertaken with greater confidence than would otherwise be possible. The recent work of Henri and Howell on the spectrum of phosgene may be cited as an example. It is clear from the work of the Zurich investigators that in the study of polyatomic molecules and the interpretation of their spectra both in the infra-red and for the visible and ultra-violet regions, the Raman effect possesses a very special utility and significance.

6. *Raman Effect and the Structure of Molecules.*

Such investigations as have been made on relatively simple substances show how remarkably the ultimate structure of the molecules comes into evidence in the Raman effect. The brilliant work of McLennan and McLeod on liquid hydrogen deserves special mention in this connection. Their observation of the alternation of the intensities of the lines in the rotational effect furnished the first experimental proof of the existence of two forms of hydrogen, a result previously anticipated by the theoretical investigations of Heisenberg and supported by Dennison's discussion of the data for specific heat. The striking experiments of McLennan, Wilhelm and Smith have subsequently shown that the slow transformation of β-hydrogen to α-hydrogen at liquid hydrogen temperatures can be studied by following the changes in the intensity of the lines in the Raman spectra over a sufficient period of time. The equally brilliant and successful researches of Rasetti in resolving the lines in the rotational effect observed with oxygen and nitrogen are also well-known. In the case of the former gas, the entire rotational spectrum consists of only alternate (odd) levels and the results are in perfect agreement with the band spectrum data and with what might be expected theoretically in the absence of a nuclear spin. In nitrogen, however, we have an alternation of intensities, the transition between even rotational levels giving the lines of greater intensity quite unlike the case of hydrogen, a result which has given rise to considerable discussion.

The unresolved rotational effect which is observed with relatively complicated molecules shows great variations in intensity from substance to substance. It was pointed out by Raman and Krishnan that these variations could be correlated with the variations of optical anisotropy of the molecules, those molecules which are highly anisotropic showing the effect strongly, and nearly symmetrical molecules to a hardly appreciable extent. Subsequent investigations have fully substantiated their remarks, and Manneback has in a recent paper shown that it has a theoretical justification.

The cases of the triatomic molecules such as N_2O, CO_2, CS_2 and SO_2 are also of great interest. By a discussion of the data for the Kerr effect, Raman and Krishnan proved conclusively in 1926 that the first three substances were non-polar. This indicates that these molecules are rectilinear in form and that their symmetric oscillations along the direction of their axes give rise to no electric moment and are therefore 'inactive' in infra-red absorption. Actually, in agreement with this conclusion, in the case of N_2O, a strong Raman line is observed which does not correspond to any infra-red absorption. In the case of CO_2 and CS_2, however, two prominent and closely situated Raman lines are observed, each of which has in addition a faint companion. From the fact that these lines are similarly polarised and do not appear in the infra-red absorption, the present writer has arrived at the conclusion that they all correspond to an inactive oscillation, the multiplet nature of which has yet to receive a theoretical explanation. In the case of SO_2 which is a polar molecule and therefore has a triangular form, we should expect three fundamental vibrations, and all these are actually observed in the Raman effect. The case of these and other polyatomic molecules has been discussed by the present writer in a recent memoir, in which the Raman effect data are utilised to determine the form of the molecules and the forces binding the atoms in them together. It was noticed in this connection that the polarisation of the Raman lines showed remarkable regularities in structurally analogous molecules, indicating a close connection between the polarisation and the geometrical character of the molecular vibrations involved. A high degree of polarisation for any Raman line is generally accompanied by relatively large intensity and corresponds to symmetrical oscillations.

7. *Raman Effect and Crystal Physics.*

The analysis of crystal structure by x-ray diffraction methods concerns itself with the determinations of the positions of the electrons and of the atoms which scatter the x-radiations. It does not tell us anything about the forces binding the atoms and electrons in the lattice together which determine the physical properties of the crystal. No doubt in the case of certain crystals, *e. g.*, rock-salt and its analogues, the assumption of a completely ionised structure suggested by the x-ray results enables the binding forces to be identified with the electrostatic attraction of the oppositely charged ions, and thus for a crystal physics to be developed on a theoretical basis. It may be questioned, however, whether the assumption of such complete ionisation is valid even in the case of all the so-called 'ionic lattices,' and there are of course an immense number of crystals for which it would be wholly beside the mark.

The Raman effect offers us a new method for studying crystals which in a sense is complementary to x-ray diffraction, for it furnishes us just the kind of information that the x-rays do not give, concerning the strength and nature of the forces which hold the crystal together. The information is of a precise character, for the lines in the Raman spectra of crystals are often extremely sharp and can be measured with great accuracy. The frequencies deduced from the spectra, and the known positions and masses of the atoms in the crystal should enable us to calculate the binding forces in the crystal.

As a typical case, we may mention that of diamond which has been studied by C. Ramaswamy and by the present writer. Diamond is a non-polar substance in which it is impossible to identify any particular group of atoms as forming an ion or a molecule. It gives a single Raman line of great intensity corresponding to a frequency of 1331·9 $cm.^{-1}$, the knowledge of which enables us to predict the specific heat and other physical properties of diamond with accuracy. Another typical case which presents a contrast to that of diamond is that of rhombic sulphur which has been studied by Krishnamurti. The x-ray analysis tells us that the crystal contains atom-complexes having the formula S_{16}, and the physical properties of the crystal suggest that many of the bonds must be weak. The fact that its Raman spectrum shows numerous lines in the extreme infra-red ranging in frequency from 84 $cm.^{-1}$ to 470 $cm.^{-1}$ is in accord with what might have been anticipated from the physical properties of the crystal.

The case of diamond shows clearly that it is not necessary for a crystal to contain "molecules" in order that it should exhibit the Raman effect. If however molecules or complex ions exist, we should expect them to give Raman lines characteristic of their internal oscillations, and in addition we may expect to observe lines indicative of 'lattice oscillations,' that is of the bodily movements of whole groups of atoms. This is actually the case. The methods which have been developed by Bär and others for studying the Raman effect in crystal powders have greatly extended the possibilities for work in this field. It is very significant that in the series of crystalline nitrates studied by Krishnamurti and by Gerlach, the frequencies characteristic of the NO_3 ions are notably influenced by the presence of the cation. This suggests that the assumption of complete ionisation in the solid crystal may be invalid.

The anisotropic structure of crystals and the anisotropy of the binding forces within them come strikingly into evidence in the Raman spectra in the remarkable character of the polarisation effects noticed and the dependence of the intensity of the lines on the setting of the crystal when polarised light is used for excitation. A beginning has been made in the study of effects of this kind by Cabannes and Daure, by Kimura and Uchida and by Menzies, but much remains to be done. Recent observations made by Krishnan and Dasgupta on the ultra-violet pleochroism of potassium nitrate crystals show an analogy to the variations of the intensity of the Raman lines with directional excitation which is so striking as to suggest a physical relationship between the two problems.

The Raman effect in crystals has also a bearing on two other fundamental problems in crystal physics, namely, the question of the existence of a " mosaic structure " in crystals and the nature of the thermal agitation in crystals. One of the most remarkable results obtained by the present writer in his investigations on diamond is that the intensity of the Raman line varies greatly with different specimens, and in one imperfect specimen, the line was distorted. It appears not unlikely that these variations may arise from the imperfections of the crystals. The influence of temperature on the Raman effect in crystals and its correlation with specific heat, thermal expansion and variation of electrical conductivity also offer an immense field for further research.

8. *Raman Effect and Physical Chemistry.*

One of the most debated problems in physical chemistry has been the question of the dissociation of electrolytes in solution. The Raman effect offers an ideal method for investigating this problem, as spectra can be obtained both for the pure substance and also for its aqueous solutions at all possible concentrations. The observed position and intensities of the lines enable us directly to determine the nature and number of the ions produced and thus to decide the question whether the dissociation is complete or only partial in strong solutions. A specially detailed investigation of this kind is that of I. R. Rao who has obtained a series of spectra of nitric acid—water mixtures and determined the positions and intensities of the lines in them. He finds that the number of HNO_3 molecules diminishes very rapidly with increasing dilutions while the NO_3 ions correspondingly increase in number. Similar results have been obtained by Nisi with sulphuric acid and its solutions. The method has also been extensively applied for the study of solutions of crystalline salts. On comparing the spectra of lithium nitrate crystals with that of the concentrated aqueous solution, Krishnamurti has found that the lattice oscillation (233 $cm.^{-1}$) which appears prominently in the spectrum of the crystal is not observed in the concentrated aqueous solution. Further, the frequencies which may be assigned to the NO_3 group are different for the crystal and for the solution, the value in the former being different for different cations, but in the latter, practically the same for all, indicating nearly complete dissociation. By studying nitrates with different content of water of crystallisation and also aqueous solutions of nitrates at different concentrations, Gerlach has obtained very interesting results. He finds that the larger the content of water of crystallisation, the more nearly does the NO_3 frequency in the crystal approach that in the aqueous solution. He also finds small differences between concentrated and dilute solutions. Taken as a whole, the results support the idea of complete dissociation even in concentrated solution, but there is room for closer investigation of the problem. Krishnamurti has made the interesting observation that mercuric chloride which dissolves in water and methyl alcohol, but does not conduct electricity, continues to exhibit the Raman lines in solution, though considerably broadened, showing that it is not appreciably ionised. He has also noticed that the line characteristic of the inactive oscillation of the NO_3 ion of the nitrates which is sharp in the crystal becomes appreciably diffuse in aqueous solution.

Other problems for which the Raman effect affords an ideal method of investigation are those connected with molecular association and polymerisation. As an instance of its application, the case of sulphur trioxide liquid studied by the present writer may be quoted. At room temperatures, this substance gives nine Raman lines, of which six weaken or disappear with rise of temperature and may therefore be attributed to S_2O_6, and the remaining three brighten up correspondingly which are therefore ascribable to SO_3 molecules. Another liquid, which has been much studied in view of its great importance, is water. Change of temperature and the presence of dissolved substances produce noticeable changes in its Raman spectrum. Interesting results have also been recently obtained at Calcutta by Parthasarathy with acetic acid and formic acid liquids. These are well known to be highly associated liquids and the break-up of molecular association with rise of temperature is indicated by the disappearance of a number of Raman lines corresponding to the oscillations of low frequency. Many other examples of liquids may be quoted, the detailed study of which at different temperatures may be expected to throw light on the mechanism of molecular association. Dadieu and Kohlrausch have also recently observed cases of liquid mixtures in which the Raman frequencies differ appreciably from those of the pure substances ; the effect is evidently connected with changes in molecular association in a mixture of the two substances.

Notable changes have been observed in the Raman spectra of substances when they pass from the state of vapour to liquid or from liquid to crystalline solid. As instances may be mentioned the cases of H_2S (gas and liquid) studied by the present writer and antimony trichloride (crystal and liquid) investigated by Krishnamurti. In the latter case, a remarkable broadening of the Raman lines in addition to a shift of their positions in passing from solid to the liquid state is noticed. The transformation from a liquid to a vitreous solid or from the crystalline to the glassy states of the same substance (*e.g.* quartz crystal to quartz glass) are other cases in which changes in Raman spectra have been observed but as yet await complete interpretation.

The knowledge of the characteristic frequencies of vibration is essential for the calculation of the thermal energy of molecules. It follows, therefore, that the theory of specific heats is another branch of physical chemistry which stands in direct relation to the Raman effect and has much to gain from its study.

9. *Raman Effect and the Nature of Valence.*

Numerous facts suggest a relationship between the Raman effect and the nature of the valency bonds. Repeated investigations fail to reveal any Raman lines in the spectrum of rock-salt corresponding to its known rest-strahlen frequency. One may conjecture that this is connected with the fact that the crystal consists of charged atoms of sodium and chlorine held together by electrostatic forces. In HCl gas and liquid we get the Raman effect, but not in an aqueous solution of HCl which presumably consists of hydrogen and chlorine ions. In aqueous solutions of salts we find no Raman lines except those corresponding to the molecules of water and the separated ions. Further, the lattice frequencies observed in certain crystals, *e.g.*, lithium nitrate, do not appear in the corresponding solutions. The inference suggests itself from these facts that the Raman effect appears most strongly when the atomic structures under consideration are bound by co-valent or homopolar bonds, and tends to weaken when these bonds change their characters and pass into heteropolar or electrovalent linkages. That this view is not conjectural but has strong evidence to support it is shown by the work of Krishnamurti who has examined a great many metallic halides in the solid crystalline state. He found that mercurous and mercuric chlorides which are known to be covalent compounds exhibit intense Raman lines and thus form a most striking contrast to the case of rock-salt and its analogues. He has discussed in great detail the results of his experiments and pointed out the close correspondence between the behaviour of crystals as regards Raman effect and the electrical conductivity of those substances just above their melting point. He finds also that the broad division between ionic and molecular crystal lattices has its counterpart in the Raman effect, the typical ionic crystals (NaCl, KCl) giving no lines, while the typical molecular substances (CCl_4, Hg_2Cl_2) show prominent lines. The various physical properties such as volatility, the power of forming stable organic derivatives, and solubility in polar or non-polar solvents which serve to distinguish the covalent from the electrovalent type of linkage also seem to distinguish the compounds which show strong Raman spectra from those which do so only with great difficulty or not at all. He has considered the position of the elements forming the halides in the periodic table and shown that Grimm's classification of the halides faithfully reflects their behaviour in respect of the Raman effect. He finally comes to the conclusion that the Raman spectra of crystals enable us to distinguish easily between the eloctrovalent and covalent types of linkages in chemical compounds.

Another important discovery of Krishnamurti which has a bearing on the present subject relates to the behaviour of paramagnetic crystals, *e.g.*, ferrous and nickel sulphates. All diamagnetic crystalline sulphates, as for example the sulphates of magnesium and zinc, give strong Raman spectra in which the frequencies attributable to the SO_4 group come out very clearly. In ferrous and nickel sulphates, however, no trace of these lines could be observed even though long exposures were given to ensure their appearance if present. In other paramagnetic sulphates as, for example those of copper and manganese, a weakening of the SO_4 lines was evident. Such paramagnetic crystalline nitrates as were studied also show a weakening of the Raman lines given by the NO_3 frequencies as compared with diamagnetic nitrates. These observations indicate that the presence of paramagnetic cations in the crystal tends to weaken or destroy the lines characteristic of the anions, and are evidently of great interest, but as yet lack a theoretical explanation. Further experimental work on a more extensive scale, especially with the salts of the rare earths and other paramagnetic compounds is evidently desirable.

An interesting question is whether any relationship exists between the Raman effect and the photochemical dissociation of molecules. There is little doubt that the electrons which take part in linking the atoms together are disturbed by light and play an important part in both phenomena, and it seems natural to expect a relationship between them. It is interesting in this connection to notice that Sirkar working at Calcutta has found that the intensity of some of the Raman lines of organic compounds increases as the wave-length of the exciting radiation is diminished, more quickly than in the ratio of the inverse fourth power of the wave-length. As the wave-length of the exciting radiation is diminished towards the ultra-violet, it comes nearer the region where the molecule can be photochemically activated, and it is perhaps not surprising that the deviations from the Rayleigh inverse fourth power law should occur.

10. *Raman Effect and Organic Chemistry.*

By far the most numerous of chemical compounds in which the homopolar or co-valent linkages play a part are those we meet with in organic chemistry. It is not surprising, therefore, that organic compounds give intense Raman spectra and offer a wealth of material suitable for the study of the Raman effect and its relation to chemical constitution. The immense variety of substances available for study make it possible to derive in an empirical way, conclusions of undoubted validity even in complicated cases in which no theoretical treatment would be possible at the present time. Two of the earliest workers in this field were Venkateswaran at Calcutta and Daure in France. Venkateswaran by himself and in collaboration with Ganesan and the present writer has examined a very large number of compounds of well-defined chemical type. Dadieu and Kohlrausch at Graz have also done an immense amount of careful work and have given a general description of their results in a recent memoir to which the attention of the reader may be invited. Venkateswaran's recent work on metallo-organic, hetero-cyclic and organic sulphur-compounds is of special interest, as indicating further avenues of research just being opened up. As yet most of the work has been done with organic liquids or solutions. Very little has been done with organic vapours or crystals. There is little doubt that a comparative study of selected substances in all the three states will be productive of important results.

By examining a homologous series of compounds commencing from its earliest member, it is possible to trace the development of the Raman spectrum with increasing complexity of the molecule and to locate those frequencies which are characteristic of particular groups or linkages. The different isomers of a chemical compound show strikingly different spectra. Much information on these and other points will be found in the papers of Bonino and Brüll, Venkateswaran, Daure and of Dadieu and Kohlrausch. The latter authors have also shown how it is possible to correlate the characteristic frequencies of certain groups with their dissociation energies. These frequencies indeed show variations within certain limits. It is of great interest to find that the chemists' classification of organic compounds into the aliphatic, aromatic and the heterocyclic classes is clearly reflected in the character of their respective spectra. By glancing for example at a chart of the spectra of hexane and of benzene, one can realise at once that the former with its numerous low frequencies must be a lengthened structure while the latter is a compact ring with relatively fewer and higher fundamental frequencies. It becomes obvious why the specific heats of aliphatic and aromatic compounds differ so appreciably. An examination of the finer features, as for instance the intensity of the unresolved rotational effect and the structure of the CH band, reveals characteristic differences between the different groups of compounds. As yet little has been done towards the study of the polarisation of the lines in the Raman spectra of organic compounds. There is little doubt that such a study would be most fruitful and lead us to a fuller insight into the chemistry of carbon compounds.

In the field of organic chemistry we have cases where the study of the Raman effect brings us into contact with other optical phenomena, *e.g.*, optical activity, colour and fluorescence. The study of these relationships, however, has not yet sufficiently advanced for detailed comment to be made upon it in the present essay. It may be mentioned that the presence of electric polarity in molecules comes out clearly in the Raman spectra. As an instance may be quoted the cases of aliphatic alcohols and fatty acids. Only in methyl alcohol is the vibration characteristic of the OH group observable, and it appears here as a broad band in the spectrum. In none of the higher alcohols or fatty acids is this oscillation to be traced. In striking contrast with this is the observation of Venkateswaran that the SH band is to be seen with equal clearness in the whole series of organic hydrosulphides.

Appendix I

Bibliography of the Raman Effect

Plan of the Bibliography.

The bibliography has been divided into 26 sections, a list of which appears below. Section A contains references to special monographs and section B to articles of a general character which have appeared dealing with the effect. Section C contains references to recently published books in which the phenomenon is discussed. In the remaining 23 sections the literature is classified under the appropriate subject headings. Papers which deal in detail with two or more aspects are listed under each of them separately. These sections are indicated by the letters A, B, C——Z, and the papers in each of them are arranged in the alphabetical order of the names of the authors (in case of joint authors, the first author) and are numbered serially.

There is an author index ; against each author are given the letters of the alphabet indicating the sections in which his name appears.

An index, arranged alphabetically, of all the substances studied is also given. In this index after each substance is given the letter indicating the section followed by the serial number of the paper from which the name of the author and the journal reference are ascertained.

The bibliography includes the papers published up to the end of June 1930.

A Special monographs.
B Journal articles.
C References in books.

D **Experimental technique.**
E Character of the lines; **continuous spectrum.**
F Intensity.
G Polarisation.
H Rotation and vibration-rotation spectra.
I Relation to infra-red absorption.
J Relation to ultra-violet absorption.
K Resonance radiation, fluorescence and phosphorescence.
L Crystals and relation to crystal structure.
M Effect of change of state.
N Effect of solution and electrolytic dissociation.
O Effect of molecular association and polymerisation.
P Liquids and liquid mixtures.
Q Influence of temperature and pressure.
R Relation to molecular structure and specific heat.
S Chemical binding and nature of valency.
T Relation to chemical constitution.
U Relation to paramagnetism and electric polarity.
V Relation to photo-conductivity and photo-chemical dissociation.
W X-ray analogue.
X Theory.
Y Incoherence.
Z Appearance in emission and absorption spectra.

A

Special Monographs.

1.	Dadieu A. and Kohlrausch, K.W.F.	Raman effect and chemistry. Ber, **63** (B) *251* (1930). General considerations. Raman frequencies of simple chemical bindings. Quantitative treatment.
2.	Joos G.	Raman effect. Handbuch der Experimental Physik. **22**, *413* (1929). Experimental arrangements. Principal results and the theory. Intensity, polarisation and coherence of the Raman lines. Raman effect in solids and gases. Constitution of solutions and organic molecules.
3.	Pringsheim P.	Raman spectra. Handbuch der Physik. **21**, *607* (1929). Typical form of the spectra. Experimental examples. Relation to infra-red bands. Homopolar molecules. Intensity. Incoherence. Polarisation. Continuous bands. X-ray analogue. Relation to the Kramers-Heisenberg dispersion theory. Rotational frequencies. Vibrational frequencies. Relation to resonance spectra.
4.	Raman C.V.	A new radiation. Ind. J. Phys., **2**. *387* (1928). Universality of the phenomenon. Line spectrum of new radiation. Nature of the new radiation. Relation to thermodynamics. Coherent or Non-Coherent radiation? X-ray analogies.
5.	Schaefer C. and Matossi, F.	The Raman effect. Fortschr. d. Chem., **20**, *1* (1930). Elementary theory of scattering. Theory of the effect. Experimental technique. Raman effect in gases and liquids, in crystals and their solutions and in organic substances. Polarisation. Intensity and the dependence on temperature.

B

Journal Articles.

1.	Bates L. F.	Important new experiments in radiation.	Sci. Prog., **23**, *392*(1929)
2.	,,	The Raman effect.	Sci. Prog., **23**, *582* (1929)
3.	,,		Sci. Prog., **24**, *385* (1930)
4.	Cabannes J.	On the experimental laws of the Raman effect.	Rev. d'Opt., 8, *461* (1929)
5.	Chwolson O.D.	Raman effect and its importance for the theory of light.	Scientia, **46**, *361* (1928)
6.	Compton A.H.	Evidence for the corpuscular character of radiation.	Rev. Mod. Phys. **1**, 74 (1929),
7.	,,	The corpuscular properties of light.	Naturwiss., **17**, *511* (1929
8.	Darrow K. K.	The scattering of light with change of frequency.	Bell system Tech. J., **8** *64* (1929).
9.	Fabry C. H.	A remarkable phenomenon in the scattering of light by transparent substances discovered by Raman.	Jour. de Phys., **9**, *92* (1928).
10.	Garner W. E. and Lennard-Jones J. E.	Molecular spectra and molecular structure.	Trans. Farad. Soc , **25**, *61* (1929).
11.	Jordan P.	The experimental basis of quantum theory.	Naturwiss, **17**, *505* (1929)
12.	Kemble E. C. and Hill E.L.	General principles of quantum mechanics Part II.	Rev. Mod. Phys., **1**, (1930).
13.	Menzies A. C.	The Raman effect.	Nature. **125**, *205* (1930).
14.	Pringsheim P.	The Raman effect.	Naturwiss. **16**, *597* (1928
15.	Raman C. V.	Presidential address.	Ind. Sci. Cong., (1929).
16.	,,	Investigations of the scattering of light.	Nature, **123**, *50* (1929).
17.	,,	Investigations of molecular structure by light scattering.	Trans. Farad. Soc., **25** *781* (1929).
18.	Rutherford E.	Raman effect and α-β-hydrogen	Proc. Roy. Soc., **A126** *184* (1930).
19.	Wood R. W.	Wave-length shifts in scattered light.	Nature, **122**, *349* (1928).
20.	...	The production of new radiations by light scattering.	J. Frank. Inst., **207** *855* (1929).
21.	...	Annual report of the Chemical Society.	(1929).

C

References in Books.

1. Born M. and Jordan P.	Elementary Quantum Mechanics.	Struktur der Materie serie Julius Springer, Berlin (1930).
2. Castelfranchi.	Fisika Moderna.	Hoepli (1930)
3. Frenkel J.	Introduction to Wave mechanics.	Julius Springer, Berlin (1929).
4. Guth E.	Handbuch der Physik.	**4**, *450-452* and *568*, Juliu Springer, Berlin (1929
5. Heisenberg W.	The Physical Principles of the Quantum Theory.	*61* (1930) S. Hirzel, Leipzig.
6. Mecke R.	Handbuch der Physik.	**21**, *509*. Julius Springer Berlin (1929).
7. Rawlins F. I.G. and Taylor A.M.	Infra-red Analysis of Molecular Structure.	*68* and *69* (1929) Camb Univ, Press.
8. Ruark A. E. and Urey H. C.	Atoms, Molecules and Quanta.	*360-368* (1930) Int. Ser Phys.
9. Schaefer C. and Matossi F.	The Infra-red Spectrum.	Struktur der Materi Series. Julius Springe Berlin (1930).
10. Sommerfeld A.	Lectures on Wave mechanics.	*88-94*, Calcutta University (1929).
11. ,,	Wave mechanics.	*174-175*, English translation. Methuen & Co London (1930).
12. Wolf K. L. and Herzfeld K.F.	Handbuch der Physik.	**20**, *555*. Julius Springer Berlin (1928).

D.

Experimental Technique.

1- Bar R.	An investigation on the Raman effect in liquids.	Helv. Phys. Acta., **2**, *154* (1929).
2. ,,	Effective optical arrangement for observing the Raman effect in liquids.	Physikal. Z., **30**, *856* (1929).
3. Daure P.	A spectrograph of great luminosity for study of visible spectra.	Rev. d'Opt., **7**, *45* (1928).
4. Dickinson R. G., Dillon R. T. and Rasetti F.	Raman spectra of polyatomic gases.	Phys. Rev., **34**, *582* (1929).
5. Gerlach W.	Raman spectra of crystalline and dissolved nitrates.	Ann. d. Phys., **5**, *196* (1930).
6. Heidt L. J. and Daniels F.	A capillary mercury vapour lamp.	J. Am. Chem. Soc., **52**, *2151* (1930).
7. Kogel G.	A new method of photographic reproduction.	Forsch. u. Fortschr., Series **5**, No. **20** (1929)
8. Krishnamurti P.	Raman effect in crystal powders of inorganic nitrates.	Ind. J. Phys., **5**, *1* (1930).
9. Langer R. M. and Meggers W. F.	Light scattering in liquids.	Bur. Stand., Jour. Res., **4**, *711* (1930).
10. Menzies A. C.	Raman effect from powdered crystals.	Nature, **124**, *511* (1929).
11. Petrikaln A. and Hochberg J.	Raman effect in high-melting substances.	Z. f. Phys., **59**. *114* (1930).
12. Rasetti F.	Further investigations on incoherent scattering in gases.	Nature, **124**, *93* (1929).
13. Reynolds N. B. and Benford F.	An apparatus for the demonstration of the Raman effect in liquids.	Rev. Sci. Inst., **1**, *415* (1930).
14. Wood R. W.	The Raman spectra of scattered radiation.	Phil. Mag., **6**, *729* (1928)
15. ,,	Improved technique for excitation of the Raman effect with special reference to gases.	J. Frank. Inst., **208**, *617* (1929).
16. ,,	The Raman effect by helium excitation.	Phil. Mag., **7**, *858* (1929).
17. ,,	Improved method of exciting Raman spectra of scattered radiation.	Phys. Rev., **33**, *294* (1929).
18. ,,	The Raman effect in gases and liquids.	Phys. Rev., **33**. *109* (1929).

D

19.	WOOD R. W.	Methods of excitation of Raman spectra.	Trans. Farad. Soc., **25** *792* (1929).
20,	,,	,, ,, ,,	Trans. Farad. Soc., **26** *99* (1930).
21.	,,	Raman spectra excited by the helium hot cathode arc and a new type of tube for small volumes of liquid.	Phys. Rev., **35**, *67* (1930).
22.	ZAHRADNICEK J. AND VLACH B.	A simple method of observing the Raman effect in liquids.	Z. f. Phys., **60**, *40* (1930).

E.

Character of the lines; Continuous Spectrum.

1. BAR R.	An investigation of the Raman effect in liquids.	Helv.Phys. Acta., **2**. *1* (1929).
2. CABANNES J.	Degradation of light frequencies by molecular scattering.	Trans. Farad. Soc., *800* (1929).
3. CABANNES J. AND DAURE P.	Spectroscopic analysis of monochromatic light scattered by fluids.	Compt. Rend., **186**, *15* (1928).
4. CABANNES J. AND SALVAIRE P.	Widening and displacement of spectrum lines by molecular scattering.	Compt. Rend., **188**, *9* (1929).
5. DABADGHAO W. M.	Raman spectra under high dispersion,	Ind. J. Phys., **5**, (1930).
6. GERLACH W.	On the breadth of the Raman lines—scattering from benzene.	Ann. d. Phys., **1**. (1929).
7. LANGER R. M. AND MEGGERS W. F.	Light scattering in liquids.	Bur. Stand. Jour. R **4**. *711* (1930).
8. ,,	Combination scattering in liquids.	Phys. Rev., **33**, (1929).
9. NIELSEN J. R.	The molecular scattering of light.	Science, **69**, *15* (1929
10. PAL N. N. AND SEN GUPTA P. N.	Raman effect in some organic and inorganic substances.	Ind. J. Phys., **5**, (1930).
11. VENKATESWARAN S.	The Raman effect in highly viscous liquids.	Nature, **122**, *506* (192
12. WOOD R. W.	Note on Raman lines under high dispersion.	Phil. Mag., **6**, (1928).

F

Intensity.

1. Daure P.	Studies on the Raman effect. in liquids	Compt. Rend., **187**, *826* (1928),
2. ,,	Photometric study of the Raman effect.	Compt. Rend., **188**, *1605* (1929),
3. Landsberg G. and Wulfsohn K.	Molecular scattering of light in solids III. Intensity of light scattered by crystalline quartz.	Z. f. Phys., **58**, *95* (1929),
4. Ornstein L. S. and Rekveld J.	Intensity measurements in the Raman effect of CCl_4 and the distribution law of Maxwell and Boltzmann.	Phys. Rev., **34**, *720* (1929 and Z. f. Phys., **57**, *539* (1929
5. ,,	On the frequency relation of the Raman lines.	Z. f. Phys., **61**, *593* (1930)
6. Rao I. R.	Raman effect in water.	Nature, **125**, *600* (1930),
7. Sirkar S. C.	On the intensities of the lines in Raman spectra.	Ind. J. Phys., **5**, *159* (1930).

G

Polarisation.

1.	Bhagavantam S.	Polarisation of the lines in Raman spectra.	Ind. J. Phys., **5**, *59* (1930).
2.	Cabannes J.	Depolarisation of scattered radiation.	Compt. Rend., **187**, *654* (1928).
3.		On the secondary radiations scattered by quartz.	Compt. Rend., **188**, *249* (1929).
4.		On the secondary radiations scattered by iceland spar.	Compt. Rend., **188**, *1041* (1929).
5.		Polarisation of Raman radiations in liquids and crystals.	Trans. Farad. Soc., **25**, *813*, (1929).
6.	Carrelli A., Pringsheim P. and Rosen B.	On the Raman effect in aqueous solutions and on the polarisation of the Raman lines.	Z. f. Phys., **51**, *511* (1928).
7.	Daure P.	Studies on the Raman effect.	Compt. Rend., **186**, *1833* (1928).
8.	Krishnamurthy P. V.	Studies on the Raman spectra.	Thesis, Calcutta University, 1929.
9.	Lindemann F.A., Keeley T. C. and Hall N.R.	Frequency change in scattered light.	Nature, **122**, *921* (1928).
10.	Menzies A.C.	Polarisation of Raman lines.	Phil. Mag., **8**, *504* (1929).
11.	Pokrowski G. I. and Gordon E. A.	Relationship between intensity, polarisation and angle of scattering for Raman radiation.	Ann. d. Phys., **4**, *488* (1930).
12.	Raman C. V. and Krishnan K. S.	Polarisation of scattered light quanta.	Nature, **122**, *169* (1928).
13.	Ramaswamy C.	Raman effect in diamond.	Ind. J. Phys., **5**, *97* (1930),
14.	Venkateswaran S.	A study of the Raman effect in glycerine and glycerine-water mixtures.	Ind. J. Phys., **3**, *105* (1928).
15.	,,	Raman spectra in organo-metallic and heterocyclic compounds.	Ind. J. Phys., **5**, *145* (1930).

H

Rotation and Vibration-Rotation Spectra.

1.	Dickinson R.G., Dillon R. T. and Rasetti F.	Raman spectra of polyatomic gases.	Phys. Rev., **34**, *582* (1929).
2.	McLennan J.C. and McLeod J. H.	On the Raman effect with liquid oxygen and with liquid nitrogen.	Trans. Roy. Soc. Canada, **22**, *413* (1928).
3.	,,	The Raman effect with liquid oxygen, nitrogen and hydrogen.	Nature, **123**, *160* (1929).
4.	McLennan J.C. Smith H. D. and Wilhelm J. O.	Raman effect in liquid α- and β-hydrogen.	Trans. Roy. Soc. Canada, **23**, *247* (1929).
5.	Raman C. V. and Krishnan K. S.	Molecular spectra in extreme infra-red.	Nature, **122**, *278* (1928).
6.	,,	Rotation of molecules induced by light.	Nature, **122**, *882* (1928).
7.	,,	The production of new radiations by light scattering. Part I.	Proc. Roy. Soc., **122**, *23* (1929).
8.	Rasetti F.	On the Raman effect in diatomic gases.	Proc. Nat. Acad. Sci., **15**, *234* (1929).
9.	,,	Incoherent scattering and structure of diatomic molecules.	Phys. Rev., **34**, *548* (1929).
10.	,,	Raman effect in diatomic molecules.	Il Nuovo Cimento, **6**, *356* (1929).
11.	,,	Alternating intensities in the spectrum of nitrogen.	Nature, **124**, *792* (1929).
12.	,,	The rotation Raman spectra of nitrogen and oxygen.	Z. f. Phys., **61**, *598* (1930).
13.	Wood R. W. and Dieke G. H.	Raman effect in HCl gas.	Phys. Rev., **35**, *1355* (1930).

I

Relation to Infra-Red Absorption.

1. Bailey C. R.	The Raman and infra-red spectra of carbon dioxide.	Nature, **123**, *410* (1929).
2. Barnes R. B.	Fine structure of infra-red absorption in organic compounds and the Raman effect.	Nature, **124**, *300* (1929). and phys. Rev., 35, 1524 (1930).
3. Bleeker C. E.	Raman effect in xylol.	Z. f. Phys., **50**, *781* (1928).
4. Bonino G. B.	Remarks on the infra-red spectrum of some halogen compounds.	Z. f. Phys., **54**, *803* (1929).
5. ,,	On the infra-red bands of hydrogen combined with carbon in the molecule of organic compounds.	Trans. Farad, Soc., **25**, *876* (1929).
6. Coblentz W. W.	The Raman spectra of scattered radiation.	Phil. Mag., **7**, *203* (1929).
7. Coblentz W. W. and Stair R.	The infra-red absorption spectrum of carbon tetrachloride as related to the Raman spectrum of scattered radiation.	Phys. Rev., **33**, *1092* (1929).
8. Czerny M.	The Raman effect of quartz.	Naturwiss., **17**, *12* (1928).
9. ,,	On the Raman effect in quartz.	Z. f. Phys., **53**, *317* (1929).
10. Ellis J. W.	An apparently anomalous Raman effect in water.	Nature, **123**, *205* (1929).
11. ,,	Vibration spectrum of ammonia molecule.	J. Frank. Inst., **208**, *507* (1929).
12. ,,	Molecular absorption spectra of liquids below 3μ.	Trans. Farad. Soc., **25**, *888* (1929).
13. ,,	The near infra-red spectrum of calcite.	Proc. Nat. Acad. Sci., **16**, *315* (1930).
14. ,,	Doublets in the vibration spectrum of cyclohexane.	Phys. Rev., **35**, *437* (1930).
15. ,,	Spectroscopic evidence of two types of ammonia molecule.	Phys. Rev., **35**, *595* (1930).
16. Ganesan A. S. and Venkateswaran S.	The Raman effect in carbon disulphide.	Nature, **124**, *57* (1929).

I

17. Hollaender A. and Williams J. W.	Molecular scattering of light from solids: plate glass.	Phys. Rev., **34**, *380* (1929).
18. Kimura M. and Uchida Y.	The Raman spectra of certain substances.	Jap. J. Phys., **5**. *97* (1928).
19. Krishnamurti P.	Raman spectrum and infra-red absorption of sulphur.	Ind. J. Phys., **5**, *105* (1930).
20. Langer R. M.	Incoherent scattering.	Nature, **123**, *345* (1929)
21. ,,	Incoherent scattering in Rochelle salt.	Phys. Rev., **33**, *1100* (1929).
22. Lecomte J.	The infra-red spectra of liquids.	Trans. Farad. Soc., **25**, *864* (1929).
23. Marvin H. H.	Combination bands in the infra-red spectra of CCl_4 and $SiCl_4$,	Phys. Rev., **33**, *952* (1929).
24. Pokrowski G.I.	On tho light scattering in water.	Z. f. Phys., **52**, *448* (1928).
25. Pringsheim P. and Rosen B.	On the Raman effect.	Z. f. Phys., **50**, *741* (1928).
26. Raman C. V.	A new radiation.	Ind. J. Phys., **2**, *387* (1928).
27. Raman C. V. and Krishnan K. S.	A new class of spectra due to secondary radiation, part 1.	Ind. J. Phys., **2**, *399* (1928).
28.	A new type of secondary radiation.	Nature, **121**, *501* (1928).
29. Raman C. V,	A change of wave-length in light scattering.	Nature, **121**, *619* (1928).
30. Raman C. V. and Krishnan K. S.	The optical analogue of Compton effect.	Nature, **121**, *711* (1928).
31.	The negative absorption of radiation.	Nature, **122**, *12* (1928).
32.	Molecular spectra in the extreme infra-red.	Nature, **122**, *278* (1928).
33. Rasetti F.	Raman effect in gases.	Nature, **123**, *205* (1929).
34. Robertson R.	Infra-red spectra.	Nature, **123**, *915* (1929)
35. ,,	Infra-red spectra of gases.	Trans. Farad. Soc., **25**, *899* (1929).

I

36. ROBERTSON R. AND FOX J. J.	Infra-red absorption of diamond by infra-red spectrometer and Raman methods.	Nature, **125**, *704* (1930).
37. ROCARD Y.	New scattered radiations.	Compt. Rend., **186**, *1107* (1928).
38. SCHAEFER C.	Infra-red spectra of solid bodies.	Trans. Farad. Soc., **25**, *841* (1929).
39. ,,	Raman effect and infra-red spectrum for carbon tetrachloride and silicon tetrachloride.	Z.f. Phys., **60**, *586* (1930).
40. SCHAEFER C. AND BORMUTH C.	The infra-red absorption spectrum of sodium nitrate.	Z. f. Phys., **62**, *508* (1930)
41. SNOW C. P.	Relation between Raman lines and infra-red bands.	Phil. Mag., **8**, *369* (1929)
42. ,,	Excited radicals in chemical compounds.	Phys. Rev., **35**, *563* (1930).
43. ,,	Infra-red investigations of molecular structure—Part V. The simplest kind of polyatomic molecule.	Proc, Roy. Soc., **128 A**, *294* (1930).
44. TAYLOR A. M.	The Raman effect of some AX_4 groups.	Trans. Farad. Soc., **25**, *830* (1929).
45. WOOD R. W.	Raman lines from hydrochloric acid gas.	Nature, **123**, *166* (1929).
46. ,,	The Raman effect with hydrochloric acid gas. 'The missing line'.	Nature, **123**, *279* (1929).
47.	The Raman effect in gases, I. HCl and NH_3.	Phil. Mag., **7**, *744* (1929),

J

Relation to Ultra-violet Absorption.

1. Babcock H. D.	A new absorption band of atmospheric oxygen and the vibrational frequency of the normal molecule.	Phys. Rev., **35**, *125* (1930).
2. Henri V. and Howell O. R.	The structure and activation of the phosgene molecule-Parts I, II and III.	Proc. Roy. Soc., **A 128**, *178* (1930).
3. Langseth A.	A Relation between Raman spectra and ultra-violet absorption.	Nature, **124**, *92* (1929).
4. McLennan J. C.	On the Raman effect with liquid oxygen, nitrogen and hydrogen.	Trans. Farad. Soc., **25**, *797* (1929).

K

Resonance Radiation, Fluorescence and Phosphorescence.

1. BHAGAVANTAM S.	Raman effect in relation to crystal structure and properties of diamond.	Ind. J. Phys., **5**, 169 (1930).
2. COTTON A.	Remarks on the note of Cabannes and Daure on molecular scattering.	Compt. Rend., **186**, *1475* (1928).
3. DAS P.	Raman effect and fluorescence.	Nature, **123**, *607* (1929).
4. ,,	Raman and resonance radiations.	Z. f. Phys., **63**, *224* (1930).
5. POSEJPAL V.	Fluorescence of benzene and its infra-red absorption.	Compt. Rend., **187**, *1046* (1928).
6. ,,	Fluorescence and infra-red absorption.	Compt. Rend., **189**, *159* (1929).
7. RAMASWAMY C.	The Raman effect in diamond.	Ind. J. Phys., **5**, *97* (1930).
8. RASETTI F.	On a fluorescence spectrum of oxygen.	Proc. Nat. Acad. Sci., **15**, *411* (1929).
9. SAHA M. N., KOTHARI D. S. AND TOSHNIWAL G. R.	Negatively modified scattering.	Nature, **122**, *398* (1928).
10. SHAPIRO C. V.	Raman spectrum and fluorescence of benzene.	Nature, **124**, *372* (1929).
11. WAWILOW S. J. AND TUMMERMANN L. A.	A noteworthy case of photoluminescence of liquids.	Z. f. Phys., **54**, *270* (1929).

L

Crystals and Relation to Crystal Structure.

1. BAR R.	Raman effect from powdered crystals.	Nature, **124**, *692* (1929).
2. BHAGAVANTAM S.	Relation of Raman effect to crystal structure and properties of diamond.	Ind. J. Phys., **5**, *169* (1930).
3. DICKINSON R. G. AND DILLON R.T.	The Raman spectrum of gypsum.	Proc. Nat. Acad. Sci., **15**, *695* (1929).
4. GERLACH W.	Raman spectra of crystalline and dissolved nitrates.	Ann. d. Phys., **5**, *196* (1930).
5. GROSS E. AND ROMANOVA M.	On light-scattering in quartz and solid amorphous bodies containing the SiO_2 group.	Z. f. Phys., **55**, *744* (1929).
6. KIMURA M. AND UCHIDA Y.	Raman spectra of calcite, aragonite and water solution of potassium carbonate.	Sci. Pap. Inst. Phys. Chem. Res., Tokyo., **11**, *199* (1929).
7. KORNFELD H.	Remark on the paper by G. Landsberg and L. Mandelstam, " A phenomenon in light-scattering in crystals."	Naturwiss., **16**, *653* (1928).
8. KRISHNAMURTI P.	Raman effect in crystal powders of inorganic nitrates.	Ind. J. Phys.,**5**, *1* (1930).
9.	Raman spectrum and infra-red absorption of sulphur.	Ind. J. Phys., **5**, *105* (1930).
10.	Raman effect in metallic halides.	Nature, **125**, *892* (1930).
11.	Raman spectra of crystalline inorganic chlorides.,	Ind. J. Phys., **5**, *113* (1930).
12.	Raman effect in some crystalline inorganic sulphates. Influence of paramagnetism.	Ind. J. Phys., **5**, *183* (1930).
13. KRISHNAN K. S.	The Raman effect in crystals.	Nature, **122**, *477* (1928).
14. ,,	The Raman spectra of crystals.	Ind. J. Phys., **4**, *131* (1929).
15. LANDSBERG G. AND MANDELSTAM L.	A new observation on light-scattering in crystals.	Naturwiss., **16**, *557* (1928).
16. ,,	On a new fact relating to the scattering of light in crystals.	Compt. Rend., **187**, *109* (1928).
17. ,,	A new observation on the light-scattering in crystals.	Naturwiss., **16**, *772* (1928).
18. ,,	On light-scattering in crystals.	Z. f. Phys., **50**, *769* (1928).
19. ,,	A new phenomenon in light-scattering.	J. Russ. Phys. Chem. Soc., **60**, *335* (1928).

L

20. Menzies A. C.	Raman effect from powdered crystals.	Nature, **124**, *511* (1929)
21. Nisi H.	Raman effect in crystals.	Proc. Imp. Acad. Tokyo, **5**, *127* (1929).
22. ,,	Raman effect in some crystals.	Proc. Imp. Acad, Tokyo, **5**, *407* (1929).
23. Raman C. V.	A new radiation.	Ind. J. Phys., **2**, *387* (1928).
24. Ramaswamy C.	Raman effect in diamond.	Nature, **125**, *704* (1930).
25. Rao I. R.	The Raman effect in crystals.	Ind. J. Phys., **3**, *123* (1928).
26. Schaefer C., Matossi F. and Aderhold H.	Raman effect in crystals.	Physikal. Z., **30**, *581* (1929).

M

Effect of Change of State.

1. Daure P.	A study of the Raman effect in some liquefied gases.	Trans. Farad. Soc., **25**, *825* (1929).
2. Krishnamurti P.	Raman spectra of crystalline powders.	Nature, **125**, *463* (1930).
3. ,,	Raman spectra of crystalline inorganic chlorides.	Ind. J. Phys., **5**, *113* (1930).
4. Mecke R.	General discussion on Raman effect.	Trans. Farad. Soc., **25**, *839* (1929).
5. Ramdas L. A.	The Raman effect in gases and vapours.	Ind. J. Phys., **3**, *131* (1928).
6. Salant E. O. and Sandaow A.	On the vibration frequencies of HCl and HBr in the liquid state.	Phys. Rev., **35**, *214* (1930).

N

Effect of Solution and Electrolytic Dissociation.

1. Bell R.M. and Fredrickson W.R.	Raman effect in sulphuric acid.	Nature, **125**, *892*(1930).
2. Carrelli H., Pringsheim P. and Rosen B.	Raman effect in aqueous solutions and the polarisation of the Raman lines.	Z. f. Phys. **51**, *511*, (1928).
3. Daure P.	Experimental contribution to the study of Raman effect.	Ann. de physique, **12**, *375* (1929).
4. Dickinson R. G. and Dillon R. T.	Raman spectra of solutions of some ionised substances.	Proc. Nat. Acad. Sci., **15**, *334* (1929).
5. Gerlach W.	The Raman spectrum of crystalline and dissolved nitrates.	Naturwiss., **18**, *182* (1930).
6. ,,	Raman spectra of crystalline nitrates.	Nature, **125**, *819* (1930).
7. ,,	Raman spectra of crystalline and dissolved nitrates.	Ann. d. Phys., **6**, *196* (1930).
8. ,,	On the Raman bands of water.	Physikal, Z., **31**, *695* (1930).
9. Harkins W. D., Gans D. M. and Bowers H. E.	Raman effect for solutions of sulphur dioxide.	Nature, **125**, *464* (1930)
10. Hollaender A. and Williams J. W.	The molecular scattering of light from solids: crystalline sulphates and their water solutions.	Phys. Rev., **34**, *994* (1929).
11. Kinsey E.L.	The effect of dilution upon the Raman spectra of nitric acid.	Phys. Rev., **35**, *284* (1930).
12. Kishi I.	Raman spectra of nitric acid and aqueous solutions of certain nitrates.	Mem. Coll. Sci., Kyoto, A **13**, *163* (1930).
13. Leontowitsch M.	Note on the spectrum of light scattered from $K_2 CO_3$ solution.	Z. f. Phys., **54**, *155* (1929).
14. Meyer E. H. L.	On the Raman bands of water.	Physikal. Z., **31**, *699* (1930).
15. Mukherjee S. K. and Sen Gupta P. N.	The Raman spectrum of sulphuric acid and the sulphates.	Ind. J. Phys., **3**, *503* (1929).
16. Nisi H.	Raman spectra of some compounds containing the S_mO_n or RO_4 group.	Jap. J. Phys., **6**, *119* (1929).

N

17. PRINGSHEIM P. AND YOST M.	Raman effect in some aqueous solutions.	Z. f. Phys., **58**, *1* (1929).
18. RAMASWAMY C.	Raman spectra of inorganic sulphates and nitrates.	Ind. J. Phys., **5**, *193* (1930).
19. RAO I. R.	Raman effect and electrolytic dissociation.	Nature, **124**, *762* (1929)
20. ,,	Study of electrolytic dissociation by the Raman effect—I. Nitric acid.	Proc. Roy. Soc., **A127**, *279* (1930).
21. WOODWARD L. A.	Raman effect of nitric acid in solution.	Nature, **126**, *58* (1930).

O

Effect of Molecular Association and Polymerisation.

1. Austin J. B.	Raman effect in liquefied gases.	Nature, **125**, *464* (1930)
2. Bhagavantam S.	Influence of polymerisation and molecular association on the Raman effect.	Ind. J. Phys., **5**, *49* (1930)
3. Dadieu A. and Kohlrausch K. W. F.	Constitution of liquid ammonia.	Naturwiss., **18**, *154* (1930)
4 Ruark A. E.	Wave-length shifts in scattered light.	Nature, **122**, *312* (1928)

P

Liquids and Liquid Mixtures.

1. BHAGAVANTAM S.	Raman spectra of some elements and simple compounds.	Ind. J. Phys., **5**, *35* (1930)
2. BHAGAVANTAM S. AND VENKATESWARAN S.	Raman effect with optically active substances.	Nature, **125**, *237* (1930)
3. BONINO G. B. AND BRULL L.	Raman effect: V.	Gazetta, **59**, *729* (1929)
4. CZAPSKA W. M.	Molecular scattering.	Compt. Rend., **189**, *32* (1929)
5. DABADGHAO W. M.	Raman spectra under high dispersion.	Ind. J. Phys., **5**, *207* (1930)
6. DADIEU A. AND KOHLRAUSCH K. W. F.	Contribution to the knowledge of Raman effect.	Physikal. Z., **30**, *384* (1929)
7. ,,	The Raman effect in water,	Naturwiss., **17**, *625* (1929)
8. ,,	The Raman effect in binary mixtures.	Physikal. Z., **31**, *514* (1930)
9. DAURE P.	Studies on the secondary radiation observed in the molecular scattering of light by liquids (Raman effect).	Compt. Rend., **186**, *1833* (1928)
10.	On the secondary radiation observed in the molecular scattering of light (Raman effect).	Compt. Rend., **187**, *940* (1928)
11.		Compt. Rend., **188**, *61* (1929)
12. ,,	Experimental contribution to the study of Raman effect.	Ann. de Physique, **12**, *375* (1929)
13. DICKINSON R. G. AND WEST S. S.	Raman spectra from sulphur dioxide.	Phys. Rev., **35**, *1126* (1930).
14. DILLON R. T. AND DICKINSON R. G.	Raman spectra from acetone.	Proc. Nat. Acad. Sci., **15**, *699* (1929).
15. FUJIOKA Y.	Raman effect in organic substances	Sci. Pap. Inst. Phys. Chem. Res. Tokyo, **11**, *205* (1929).
16. KINSEY E. L.	The Raman effect in water.	Phys. Rev., **34**, *541*(1929).

P

17.	Langer R. M.	Light scattering in liquids.	Jour. Opt. Soc. Am, (suppl.) **17**, *24* (1928).
18.	Langer R. M. and Meggers W.	Light scattering in liquids.	Bur. Stand., Jour. Res., **4**, *711* (1930).
19.	McLennan J. C., Smith H. D. and Wilhelm J. O.	Raman effect with liquid methane.	Trans. Roy. Soc. Canada, **23**, *279* (1929).
20.	Meggers W. F. and Langer R. M.	Regularity of frequency shifts in scattered light.	Phys. Rev., **33**, *287* (1929).
21.	Okubu J. and Hamada H.	Raman spectra of some organic liquids.	Sci. Rep. Tohoku, **18** *601* (1929).
22.	Petrikaln A. and Hochberg J.	On the Raman effect.	Z. Phys. Chem., **3**, *217* (1929), **3**, *405* (1929).
23.	Pringsheim P. and Schlivitch S.	Raman effect of water.	Z.f. Phys., **60**, *581* (1930).
24.	Raman C. V. and Krishnan K. S.	The production of new radiations by scattering Part I.	Proc. Roy. Soc., A**122**, *23* (1929).
25.	Rao I. R.	Ultra-violet Raman spectrum of water.	Nature, **123**, *87* (1929).
26.	Salant E. O. and Sandow A.	Raman effect for HCl liquid.	Phys. Rev., **33**, *1096* (1929).
27.	Soderqvist J.	Raman effect for some organic substances.	Z. f. Phys., **59**, *446* (1930).
28.	Venkateswaran S.	A study of the Raman effect in glycerine and glycerine water mixtures.	Ind. J. Phys., **3**, *105* (1928)
29.	,,	The Raman effect in some organic liquids.	Phil. Mag., **7**, 597 (1929).
30.	,,	Raman effect in liquid pyridine.	J. Phys. Chem., **34**, *145* (1930).
31.	Venkateswaran S. and Karl A.	The Raman effect in alcohols.	Z. Phys. Chem., **1**, *466* (1928).
32.	Whitelaw N. G.	The Raman effect of ketones.	Phys. Rev., **34**, *376* (1929)
33.	Williams J. W. and Hollaender A.	A study of the Raman effect in acetone.	Proc. Nat. Acad, Sci., **15**, *421* (1929).

Q

Influence of Temperature and Pressure

1. BRICKWEDDE F. G. AND PETERS M. F.	Temperature variations of the Raman effect in quartz.	Phys. Rev., **33**, *117*. (1929).
2. FUJIOKA Y.	Influence of temperature on Raman lines.	Nature, **124**, *11* (1929).
3.	Raman effect in organic substances.	Sci. Pap. Inst. Phys. Chem. Res. Tokyo, **11**, *205* (1929).
4. KRISHNAN K. S.	Influence of temperature on the Raman effect.	Nature, **122**, *650* (1928).
5. LANDSBERG G. AND LEONTOWITSCH M.	On the intensity and the temperature relation of the combination scattering.	Z. f. Phys., **58**, *439* (1929).
6. LANDSBERG G. AND MANDELSTAM L.	Scattering of light in crystals at high temperatures.	Z. f. Phys., **58**, *250* (1929).
7.	Scattering of light in crystals at high temperatures II.	Z. f. Phys., **60**, *364* (1930).
8. MEYER E.H.L. AND PORT T.	Raman effect in water I.	Physikal. Z., **31**, *509* (1930).
9. MEYER E.H.L.	Raman effect in water II.	Physikal. Z., **31** *510* (1930).
10.	On the Raman effect in water.	Physikal. Z., **30**, *170* (1929).
11. PARLIN W.A.	The effect of temperature on the absorption bands of fused quartz in the infra-red.	Phys. Rev., **34**, *81* (1929).
12. VENKATESWARAN S.	A study of the Raman effect in glycerine and glycerine-water mixtures.	Ind. J. Phys., **3**, *105* (1928).

R

Relation to Molecular Structure and Specific Heat.

1.	Andrews D. H.	The relation between Raman spectra and the molecular structure of organic compounds.	Phys. Rev., **35**, *662* (1930)
2.	Andrews D. H. and Southard J. C.	The calculation of the specific heats of solid organic compounds from Raman spectra.	Phys. Rev., **35**, *670* (1930)
3.	Bhagavantam S.	Raman effect and molecular structure.	Ind. J. Phys., **5**, *73* (1930)
4.	,,	Relation of Raman effect to crystal structure and properties of diamond.	Ind. J. Phys., **5**, *169* (1930)
5.	Birge R. T. and Jeppesen C. R	Moment of inertia of hydrogen from the Raman effect.	Nature, **125**, *463* (1930)
6.	Bonhoeffer K. F. and Harteck P.	Experiments on para and ortho hydrogen.	Naturwiss., **17**, *182* (1929)
7.	Henri V. and Howell O. R.	The structure and activation of the phosgene molecule. Parts I, II and III.	Proc. Roy. Soc., **A128**, *178* (1930)
8.	Kohlrausch K. W. F.	Raman spectrum and molecular structure.	Naturwiss., **18**, *527* (1930)
9.	Ramaswamy C.	The Raman effect in diamond.	Ind. J. Phys., **5**, *93* (1930)
10.	Rasetti F.	Further investigations on incoherent scattering in gases.	Nature, **124**, *97* (1929)
11.	Robertson R. and Fox J. J.	Infra-red absorption of diamond by infra-red spectrometer and Raman methods.	Nature, **125**, *704* (1830)
12.	Simon F.	Interpretation of infra-red frequencies of the diamond.	Nature, **125**, *855* (1930)
13.	Snow C. P.	Infra-red investigations of molecular structure. Part V.—The simplest kind of polyatomic molecule.	Proc. Roy. Soc., **A128**, *294* (1930)

S

Chemical Binding and Nature of Valency

1. Bonino G. B. and Brull L.	Raman spectrum and geometrical isomerism. The Raman spectra of the two forms of dichloroethylene.	Z. f. Phys., **58**, *194* (1929)
2. Daure P.	Molecular scattering. Comparative studies of the Raman spectra of some hydrogen compounds.	Compt. Rend., **188**, *1492* (1929)
3. Krishnamurti P.	Raman spectra of crystalline inorganic chlorides.	Ind. J. Phys., **5**, *113* (1930)
4. Petrikaln A.	On the application of the Raman spectra to questions of structure and bonds in organic compounds.	Z. Phys. Chem., 3, *360* (1929)
5. Reynolds N. B. and Williams J. W.	The molecular scattering of light from certain organic liquids.	J. Frank. Inst., **210**, *41* (1930)
6. Venkateswaran S.	Raman spectra of the mercaptans.	Ind. J. Phys., **5**, *219* (1930)

T

Relation to Chemical Constitution.

1.	BHAGAVANTAM S. AND VENKATESWARAN S.	Raman spectra of some organic halogen compounds.	Proc. Roy. Soc., **A127**, *360* (1930).
2.	BONINO G. B. AND BRULL L.	Studies on the Raman effect I.	Gazetta, **59**, *643* (1929).
3.	,,	Studies on the Raman effect II.	Gazetta, **59**. *660* (1929).
4.	,,	Studies on the Raman effect III.	Gazetta, **59**, *668* (1929).
5.	,,	Studies on the Raman effect IV	Gazetta, **59**, *675* (1929).
6.	,,	Raman spectrum and geometrical isomerism.	Z. f. Phys., **58**, *194* (1929).
7.	BOURGUEL M. AND DAURE P.	Chemical constitution and Raman effect.	Compt. Rend., **190**, *1298* (1930).
8.	DADIEU A. AND KOHLRAUSCH K.W.F.	Studies on the Raman effect.	Sitz. Akad. Wiss. Wien, **138**, *41* (1929).
9.	,,	The Raman effect in isomeric organic substances.	Naturwiss., **17**, *366* (1929)
10.	,,	Raman effect II—Raman spectrum of organic substances III.	Monatsh. **52**, *379* (1929).
11.	,,	Raman effect IV.	Monatsh, **53** and **54**, *282* (1929).
12.	,,	Raman effect V.	Monatsh, **55**, *58* (1930).
13.	,,	Raman effect VI.	Monatsh, **55**, *201* (1930).
14.	,,	Studies on the Raman effect VII.	Sitz. Akad. Wiss. Wein, 139, *79* (1930).
15.	GANESAN A. S. AND VENKATESWARAN S.	A memoir on the Raman effect in liquids.	Ind. J. Phys., **4**, *195* (1929).
16.	GERLACH W.	Constitution of water and the Raman effect.	Naturwiss., **18**, *68* (1930).
17.	LESPIEAU AND BOURGUEL	Chemical constitution and the Raman effect.	Compt. Rend., **190**, *1504* (1930).
18.	PAL N. N. AND SENGUPTA P.N.	Raman effect of some organic and inorganic substances.	Ind. J. Phys., **5**. *13*. (1930).
19.	PETRIKALN A. AND HOCHBERG J.	The Raman spectrum of some organic and inorganic compounds.	Z. Phys. Chem., **4**, *299* (1929).

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20.	Petrikaln A. and Hochberg J.	On the Raman effect in cyanogen group.	Z. Phys. Chem. **8**, *440* (1930).
21.	TRUMPY B.	Raman effect and constitution of the molecules I.	Z. f. Phys. **62**, *806* (1930).
22.	VENKATESWARAN S.	Raman effect and chemical constitution.	Proc. Inst. Chem. (India) *98* (1929).
23.		Raman effect in some organo metallic and heterocyclic compounds.	Ind. J. Phys. **5**, *145* (1930).
24.	VENKATESWARAN S. AND BHAGAVANTAM S.	The Raman spectra of some aldehydes and mesitylene.	Proc. Roy. Soc., A128 *252* (1930).
25.		Interpretation of Raman spectra: some aliphatic amines and alcohols.	Ind. J. Phys. **5**, *129* (1930).

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Relation to Paramagnetism and Electric Polarity.

1. Ghosh P. N. and Mahanti P. C.	Molecular stucture of triatomic gases.	Physikal. Z., **30**, *531* (1929).
2. ,,	Raman effect in carbon dioxide.	Nature, **124**, *98* (1929).
3. ,,	Raman effect in gases and liquids.	Nature, **124**, *230* (1929).
4. Krishnamurti P.	Raman effect in some crystalline inorganic sulphates—Influence of paramagnetism on Raman lines.	Ind. J. Phys., **5**, *183* (1930).
5. Zahn C. T.	Evidence for quantisation from the electric polarisation of acetic acid vapour.	Phys. Rev., **35**, *1047* (1930).

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Relation to Photo-conductivity and Photochemical Dissociation.

1. BHAGAVANTAM S.	Relation of Raman effect to crystal structure and properties of diamond.	Ind. J. Phys., (1930).	**5**,	*169*
2. PAL N. N. AND SENGUPTA P. N.	Raman effect in some organic and inorganic substances.	Ind. J. Phys., (1930).	**5**,	*13*

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X-ray Analogue.

1.	Carrelli A.	The electronic Raman effect.	Z. f. Phys., **61**, *632* (1930).
2.	,,	Raman effect in the X-ray region.	Nature, **125**, *201* (1930).
3.	Coster D., Nitta I. and Thijssen W. J.	Raman effect for X-rays.	Nature, **124**, *230* (1929).
4.	Davis B. and Mitchell D. P.	Fine structure of the scattered radiation from graphite.	Phys. Rev., **32**, *331* (1928).
5.	Kast W.	Raman effect in the X-ray region.	Z. f. Phys., **58**, *519* (1929)
6.	Krishnan K. S.	The Raman effect in X-ray scattering.	Nature, **122**, *961*, (1928).
7.	Mitchell D. P.	Change of frequency of X-rays scattered by bound electrons.	Phys. Rev., **33**, *871*, (1929).
8.	Ponte M. and Rocard Y.	The Raman effect in the X-ray region.	Compt. Rend., **187**, *828* (1928).
9.	Ray B. B.	Scattering of X-rays by bound electrons.	Nature, **125**, *746* (1930).
10.	,,	Scattering of X-rays by bound electrons.	Nature, **125**, *856* (1930).

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Theory.

1. Amaldi E.	On the quantum theory of the Raman effect.	Att. Real. Acc. Naz. Rend. **9**, *876* (1929).
2. Amaldi E. and Segre E.	On the theory of the Raman effect.	Att. Real. Acc. Naz. Rend. **9**, *407* (1929).
3. Andrews D.H.	Frequency distribution in Raman spectra.	Phys. Rev., **34**, *1626* (1929).
4. Born M.	Theory of the Raman effect.	Naturwiss., **16**, *673* (1928).
5. Cabannes J.	A new optical phenomenon.	Compt. Rend., **186**, *1201* (1928).
6.	Experimental results of the Raman effect and the theory of light.	Compt. Rend., **186**, *1714* (1928).
7. Cabannes J. and Rocard Y.	The electromagnetic theory of Maxwell-Lorentz and the molecular scattering of light.	Jour. de Phys., **10**, *52* (1929).
8. Carrelli A.	A new phenomenon of scattering.	Att. Real. Acc. Naz. Rend. **8**, *155* (1928).
	A new phenomenon of scattering: Raman effect.	Att. Real. Acc. Naz. Rend. **9**, *165* (1929).
10. Darrow K. K.	Scattering of quanta with diminution of frequency.	Science, **68**, *488* (1928).
11. Dieke G. H.	Difference between the absorption and the Raman spectrum.	Nature, **123**, *564* (1929)
12- Hartley R.V.L.	A wave mechanism of quantum phenomena.	Phys. Rev., **33**, *289* (1929).
13. Heitler W. and Herzberg G.	Does the nitrogen nucleus conform with the Bose statistics?	Naturwiss., **17**, *673*
14. Hicks W. M.	The nucleus as radiator.	Phil. Mag., **8**, *108* (1929).
15. Hill E.L. and Kemble E.C.	On the Raman effect in gases.	Proc. Nat. Acad. Sci., **15**, *387* (1929).
16. Kemble E. C. and Hill E.L.	Note on the Raman effect in gases.	Phys. Rev., **33**, *1096* (1929).

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17.	KENNARD E.H.	The classical theory of the Raman effect.	Phys. Rev., **33**, *289* (1929).
18.	KRONIG R. L.	The anomalous behaviour of the nitrogen nuclei.	Naturwiss., **18**, *205* (1930).
19.	LANGER R. M.	The theory of incoherent scattering.	Phys. Rev., **33**, *1097* (1929).
20.	LEONTOWITSCH M.	Theory of polarisation of scattering in crystals.	Z. f. Phys., **61**, *548* (1930).
21.	MAJUMDAR R.C. and KOTHARI D.S.	'Common third level' in Raman effect.	Nature., **125**, *165* (1930)
22.	MANDELSTAM L, LANDSBERG G. and LEONTOWITSCH M.	Theory of molecular scattering of light in crystals.	Z. f. Phys., **60**, *334* (1930).
23.	MANNEBACK C.	The intensity of secondary scattering.	Naturwiss., **17**, *364* (1929).
24.	,,	The intensity and polarisation of coherent and incoherent radiations from diatomic molecules.	Z. f. Phys., **62**, *224* (1930).
25.	,,	Optical anisotropy and theoretical intensities of Raman lines in diatomic gases.	Nature., **125**, *88* (1930).
26.	MUSKAT M.	Dispersion formula and Raman effect for the symmetrical top.	Phys. Rev., **35**, *1262* (1930).
27.	OLDENBERG O.	Collision and radiation.	Z. f. Phys., **51**, *605* (1928).
28.	PLACZEK G.	Theory of the Raman effect.	Z. f. Phys., **58**, *585* (1929).
29.	PODOLSKY B.	Raman effect in atomic hydrogen.	Nature, **123**, *761* (1929)
30.	PODOLSKY B. and ROJANSKY V.	Smekal—Raman effect in hydrogen-like atoms.	Phys. Rev., **34**, *1367* (1929).
31.	RAMAN C. V.	A new radiation.	Ind. J. Phys., **2**, *387* (1928).
32.	RASETTI F.	Selection rules in the Raman effect.	Nature, **123**, *757* (1029).
33.	ROCARD Y.	The molecular models and the classical and quantum theory of scattering: Raman effect.	Jour. de Phys., **9**, *104S* (1928).

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34. Rossi B.	The Raman effect.	Il Nuovo Cimento, **6**, *LXI* (1929).
35. ,,	Raman effect and negative absorption.	Att. Real. Acc. Naz. Rend., **9**, *319* (1929).
36. Schaefer C.	A note on the Raman effect.	Z. f. Phys., **54**, *153* (1929).
37. Segre E.	Quantum theory of fluorescence.	Att. Real. Acc. Naz. Rend., **9**, *887* (1929).
38. Smekal A.	Quantum theory of scattering and dispersion.	Naturwiss., **16**, *612* (1928).
39. Tamm I.	Quantum theory of molecular scattering of light in solid bodies.	Z. f. Phys., **60**, *345* (1930).
40. Van Vleck J.H.	Vibrational selection principles in the Raman effect.	Proc. Nat. Acad. Sci., **15**, *754* (1929).

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Incoherence.

1.	Bogros A. and Rocard Y.	Some remarks on the Cabannes-Daure effects.	Compt. Rend. ,**186**, *1712* (1928).
2.	,,	The fine structure of the rays scattered at critical opalescence. The Cabannes-Daure effect.	Jour. de Phys., **10**, *72* (1929).
3.	Martin W. H.	Wave length shifts in scattered light.	Nature, **122**, *506* (1928).
4.	Ruark A. E.	Wave length shifts in scattered light.	Nature, **122**, *312* (1928).
5.	Ziemecki S. L. and Narkiewicz-Jodko K.	Raman effect near the critical point.	Naturwiss., **17**, *876* (1929).
6.	,,	The Raman effect in the proximity of the critical point.	Phil. Mag., **9**, *299* (1930).

Z.

Appearance in Emission and Absorption Spectra.

1. Allen H. S.	Light scattering and the hydrogen spectrum.	Nature, **123**, *127* (1929).
2. ,,	Raman lines in the spectrum of the electric discharge.	Trans. Farad. Soc., **25**, *829* (1929).
3. Boryschanskaja F. and Landsberg G.	Combination scattering in absorption and Fraunhofer lines.	Naturwiss., **18**, *183* (1930).
4. Deodhar D. B.	Raman effect and hydrogen spectrum.	Z. f. Phys., **57**, *570* (1929).
5. Finkelnburg W.	Raman effect and hydrogen spectrum.	Z. f. Phys., **58**, *425* (1929).
6. Kaplan J.	Raman lines in spectrum of electric discharge.	Phys. Rev., **34**, *1393* (1929).
7. Kothari D. S.	A possible origin of faint Fraunhofer lines.	Nature, **124**, *90* (1929).
8. Mecke R. and Wildt R.	The spectrum of sun's corona.	Z. f. Phys., **59**, *501* (1930).
9. Ramdas L. A.	The Raman effect and the spectrum of zodiacal light.	Nature, **122**, *57* (1928).
10. Saha M. N., Kothari D. S. and Toshniwal G. R.	Negatively modified scattering.	Nature, **122**, *398* (1928).
11. Venkatesachar B. and Sibaiya L.	Raman spectra in atmospheres surrounding metallic arcs.	Nature, **124**, *838* (1929).
12. Wood R. W.	Raman lines of mercury in arc improbable	Nature, **125**, *464* (1930).

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   ,,   ,,   (anhyd.), N 6, 7.
   ,,   ,,   (aq.), L 8; N 6, 7.
   ,,   sulphate (aq.), N 16.

M

Magnesium nitrate (cryst.), L 8.
   ,,   sulphate (cryst.), L 12.
   ,,   ,,   (aq.), N 15, 16, 18.
Manganese nitrate (cryst.), L 8.
Manganous sulphate (cryst.), L 12.
Menthone, P 3.
Mercuric chloride (cryst.), L 10, 11; S 3.
   ,,   (soln.), L 11.
   cyanide (soln.), T 20.
   nitrate (cryst.), L 8.
   ,,   (aq.), N 12.
   sulphate (cryst.), L 12.
Mercurous chloride (cryst.), L 10, 11.
   ,,   nitrate (cryst.), L 8.
Mesitylene, T 24.
Methane (liq.), M 1; P 11, 19.
   ), H 1.
Methyl acetate, P 6; T 8, 9.
   ,,   ,,   (mixt.), P 8.
Methyl alcohol, D 14; I 27; P 8, 17, 31; Q 3; T 14, 15, 25.
Methyl amine, T 25.
   ,,   (aq.), T 14.
Methyl benzoate, T 13.
Methyl bromide, T 14.
   ,,   chloride, T 14.
Methyl cyanacetate, S 4; T 19.
   ,,   cyanide, P 22; S 4; T 13, 18-
Methylene bromide, R 8.
Methylene chloride, I 4, 25; S 4; T 1, 12.
Methylene iodide, R 8.
Methyl ethyl ketone, P 6, 32; T 10, 15.
Methyl formate, T 14.
Methyl iodide, T 14.
   ,,   mercaptan, S 6.
   ,,   propyl ketone, T 15.
   ,,   sulphocyanide, T 20.

N

Naphthalene (cryst.), L 1.
   ,,   (melt.), P 22.
   ,,   (soln.), P 6, 22; T 10.
Neodymium ammonium nitrate (aq.), I 18.
Nickel sulphate (cryst.), L 12.
Nitric acid (aq.), L 26; N 2, 11, 12, 19, 20, 21; T 15.
Nitric oxide (gas), D 12; H 9, 10; I 42.
Nitrobenzene, Q 3; T 10, 15.
   ,,   (mixt.), P 8.
Nitrogen (gas), H 8, 9, 10, 11, 12; I 41; X 32.
Nitrogen (liquid), H 2, 3; J 4.
Nitromethane, P 22; S 4; T 14, 15.
   ,,   (mixt.), P 8.
Nitrotoluene (meta.), T 15.
   ,,   (ortho), T 15.
   ,,   (para), T 15.
Nitrous oxide (gas), H 1; I 43.

O

Octane, T 3, 15.
Oxygen (gas), H 8, 9, 10, 12; I 41; K 8; X 32.
Oxygen (liq.), H 2, 3; J 4; P 11.

P

Paraldehyde, G 10; T 19, 24.
Pentachlorethane, T 2.

Pentane, I 28; P 6; T 3, 8, 15.
Perchloric acid (aq.), I 44; N 4, 16.
Phenol, Q 3; T 10, 15, 19.
Phenol (Mixt.), Y 1, 3.
Phenyl hydrazine, T 18.
Phenyl isothiocyanate, T 18, 20.
Phenyl methyl ether, T 15.
Phosgene, J 2.
Phosphoric acid, N 16.
Phosphorus (solid), P 1.
Phosphorus pentachloride (cryst), S 3.
Phosphorus tribromide, G 5; P 10.
Phosphorus trichloride, F 1, 2; G 1, 5; P 1, 10, 12.
Picoline, P 21.
Pinene (*d* and *l*), P 2, 3.
Piperidine, T 5.
Potassium bicarbonate (aq.), N 4.
Potassium carbonate (aq.), L 6; N 4, 13; T 15.
,, cyanate (aq.), T 18.
,, cyanide (aq.), T 18, 19.
,, hydrogen selenite (aq.), N 17.
,, hydrogen sulphate (aq.), N 16.
,, iodate (aq.), N 16.
,, Nitrate (cryst), D 10; L 8; N 6, 7.
,, ,, (aq.) I 44; N 12, 18.
,, periodate (aq.), N 16.
,, pyrosulphate, N 16.
,, sulphate (aq.), I 44; N 10, 16, 18.
,, ,, (cryst.), L 12.
,, sulphite (aq.), N 4, 16.
,, thiocyanate (aq.), T 14, 18, 20.
,, tungstate (aq.), N 16.
Propane (liq.), M 1.
Propionaldehyde, T 12.
Propionic acid, P 6, 29; T 8, 9, 15.
Propyl alcohol, T 15, 21, 25.
Propyl alcohol (iso.), T 15, 21.
Propyl bromide, P 27; T 1, 12.
Propyl chloride, P 27; T 1, 12.
,, ,, (iso), T 1.
Propyl mercaptan, S 6.
Pyridine, P 21, 22, 30; S 4; T 5, 15.
Pyrrole, T 23.
Pyruvic acid, T 14.

Q

Quartz, B 19; D 14; E 4; F 3; G 3, 5, 10; I 8, 9, 25; L 5, 13, 14, 15, 16, 18, 21, 22, 25; Q 1, 5, 6, 7, 11; X 20, 22, 23.
,, (amorph), L 5.
Quinoline, T 15.

R

Rochelle salt, I 21.

S

Salicylaldehyde, T 24.
Selenious acid (aq.), N 17.
Silicon tetrachloride, G 1; I 23, 25, 39; P 1, 10, 12.
Silver nitrate (cryst.), L 8; N 6, 7.
Silver potassium cyanide (aq.), T 18, 20.
Sodium acetate (aq.), T 12.
,, arsenate (aq.), N 16.
,, bromate (aq.), N 4.
,, carbonate (aq.), T 15.
,, chlorate (cryst.), G 5.
,, ,, (aq.), N 4.
,, chloride (cryst.), D 14; I 38; L 1; N 2; X 36.
,, chromate (aq.), N 16.
,, dihydrogen phosphate (aq.), N 16.
,, dithionate (aq.), N 17.
,, molybdate, N 16.
,, nitrate (cryst.), I 40; L 1, 8, 26; N 6, 7.
,, ,, (aq.), N 2, 4, 12, 18.
,, nitrite (cryst.), L 1.
,, ,, (aq.), N 2.
,, polysulphate ($Na_2S_2O_4$), N 16.
,, ,, ($Na_2S_2O_5$), N 16.
,, ,, ($Na_2S_2O_6$), N 17.
,, potassium nitrates (eutectic), D 11.
,, selenate, N 16.
,, sulphate (cryst.), L 12.
,, ,, (aq.), I 44; N 15, 16, 18.
,, sulphite (aq.), N 16.
,, thiocyanate, T 14.
,, thiosulphate (aq.), N 16, 17.
,, tungstate, N 16.
,, vanadate, N 16.
Stannous chloride (cryst.), L 10.
Strontium nitrate (cryst.), L 8; N 7.
,, ,, (anhyd.), N 6, 7.
,, ,, (aq.), N 12, 18.
,, sulphate (cryst.), L 12.
Sulphur (cryst.), I 19, L 10.
,, dioxide (liq.), G 1; P 1, 13.
,, ,, (soln.), N 9.
Sulphuric acid, I 44; N 1, 16; T 15.
,, (aq.), I 44; L 26; N 1, 15, 16, 17.
Sulphur trioxide (liq.), G 1; O 2.

T

Telluric acid (aq.), N 16.
Tetrabromethane, T 12.
Tetrachlorethane, B 14; I 4, 25; S 4; T 12.
Tetrachlorethylene, B 14; I 25; S 4; T 12.
Tetranitromethane, T 15.
Thiophene, T 23.
Thorium chloride (cryst.), L 10.
,, nitrate (cryst.), L 8.
Tin tetrachloride, G 1; P 1, 10, 12; T 19.
Titanium tetrachloride, G 1; P 1, 10, 12.
Toluene, A 4; D 14; E 7; G 8; I 25, 27, 30; N 2; P 6, 9, 10, 24, 27; Q 2, 3; S 4; T 8, 9, 15, 19.
Tolunitrile (ortho), T 19.
Topaz, L 14, 21.
Tourmaline, L 22.
Trichlorethylene, T 2, 12.
Triethylamine, T 25.

U

Urea (aq.), T 18.
Uranium sulphate (soln.), N 17.

W

Water, A 4; D 22; F 6; G 8, 11; I 10, 18, 24, 27, 37; L 25; N 2, 5, 8, 14, 16; P 7, 9, 16, 27, 25, 31, 37; Q 8, 9, 10; T 15, 16.

X

Xylene (meta), P 4, 6; T 9, 10, 15.
,, (ortho), P 4, 6; T 9, 10, 15.
,, (para), P 4, 6; T 9, 10, 15.
,, (mixt.), D 14; I 3, 18; P 6; T 10.

Z

Zinc acetate, T 13.
,, chloride (cryst.), L 10; S 3.
,, ethyl, T 23.
,, methyl, T 23.
,, nitrate (cryst.), L 8.
,, sulphate (cryst.), L 12.
,, ,, (aq.), N 16, 18.

Appendix II

Bibliography of Earlier Papers on Light Scattering.

RAMAN C. V.	On the Doppler effect in the molecular scattering of radiation.	Nature, **103**, *165* (1919).
	On the scattering of light in the refractive media of the eye.	Phil. Mag., **37**, *568* (1919).
	On smoky quartz.	Nature, **108**, *81* (1921).
	On a method of improving the visibility of distant objects.	Nature, **108**, *242* (1921).
	On the colour of the sea.	Nature, **108**, *367* (1921).
	On the molecular scattering of light in liquids and solids.	Nature, **108**, *402* (1921).
RAY B. B.	Scattering of light by sulphur suspension.	Proc. Ind. Asoc. Cult. Sci., **7**, *1* (1921).
RAMAN C. V. AND RAY B. B.	On the transmission colours of sulphur suspensions.	Proc. Roy. Soc., **102**, *100* (1921).
RAMAN C. V.	Optical observation of the thermal agitation of the atoms in crystals.	Nature, **109**, *42* (1922).
,,	Anisotropy of molecules.	Nature, **109**, *75* (1922).
,,	Molecular structure of amorphous solids.	Nature, **109**, *138* (1922).
,,	Essay on the molecular diffraction of light.	Calcutta University Press February, 1922.
,,	Molecular aelotropy in liquids.	Nature, **110**, *11* (1922).
,,	Opalescence phenomena in liquid mixtures.	Nature, **110**, *77* (1922).
,,	Transparency of liquids and the colour of the sea.	Nature, **110**, *280* (1922).
,,	On the molecular scattering of light in water and the colour of the sea.	Proc. Roy, Soc., **101**, *64* (1922).
RAMANATHAN K. R.	On the molecular scattering of light in vapours and in liquids and its relation to the opalescence observed in the critical state.	Proc. Roy, Soc., **102**, *151* (1922).

,,	Electromagnetic theory of the scattering of light in fluids.	Proc. Ind. Asoc. Cult. Sci., **8**. *1* (1923).
Ray B. B.	The scattering of light by liquid droplets, and the theory of coronas, glories and iridiscent clouds.	Proc. Ind. Asoc. Cult. Sci., **8**, *23* (1923).
Raman C. V. and Ramanathan K. R.	The diffraction of x-rays in liquids, liquid mixtures, solutions, fluid crystals and amorphous solids.	Proc. Ind. Asoc. Cult. Sci., **8**, *127* (1923).
,,	On the molecular scattering of light in dense vapours and gases.	Phil. Mag., **45**, *113* (1923).
,,	On the molecular scattering of light in liquid mixtures.	Phil. Mag., **45**, *213* (1923).
Raman C. V. and Rao K. S.	On the molecular scattering and extinction of light in liquids and the determination of the Avagadro constant.	Phil. Mag., **45**, *625* (1923).
,,	On the polarisation of the light scattered by gases and vapours.	Phil. Mag., **46**, *426* (1932).
Ramanathan K. R.	On the colour of the sea.	Phil. Mag., **46**, *543* (1923).
Raman C. V.	Thermal opalescence in crystals and the colour of the ice in glaciers.	Nature, **111**, *13* (1923).
,,	The scattering of x-rays in liquids.	Nature, **111**, *185* (1923).
,,	A theory of the viscosity of liquids.	Nature, **111**, *532* (1923).
,,	The viscosity of liquids.	Nature, **111**, *555* (1923).
,,	The nature of the liquid state.	Nature, **111**, *428* (1923).
,,	The scattering of light by anistropic molecules.	Nature, **112**, *165* (1923).
,,	The scattering of light by liquid and solid surfaces.	Nature, **112**, *281* (1923).
Raman C. V. and Ramanathan K. R.	The molecular scattering of light in carbon dioxide at high pressures.	Proc. Roy, Soc., **104**, *357* (1923).
Ramanathan K. R.	Molecular scattering of light.	Phys. Rev., **21**, *564* (1923).
Kamesvara Rav J. C.	Molecular scattering of light in liquid mixtures.	Phys. Rev., **22**, *78* (1923).
Ramanathan K. R-	Electromagnetic theory of the scattering of light in fluids.	Proc. Ind. Asoc. Cult. Sci., **8**, *181* (1924).

Sur N. K,	Scattering of light by smoky quartz.	Proc. Ind. Asoc. Cult. Sci., **8**. *271* (1924).
Bhattacharyya D.K.	A study of the critical opalescence of carbon dioxide.	Proc. Ind. Asoc. Cult, Sci.. **8**, *277* (1924).
Kamesvara Rav J. C.	The opalescence of binary liquid mixtures.	Proc. Ind. Asoc. Cult. Sci., **9**, *19* (1924).
Raman C. V.	The structure of molecules in relation to their optical anisotropy.	Nature, **114**, *49* (1924).
Ganesan A. S.	Oblique scattering of light in gases and liquids.	Phys. Rev., **23**, *63* (1924)
Ramdas L. A.	The scattering of light by solid surfaces.	Proc. Ind. Asoc. Cult. Sci., **9**, *129* (1925).
Ganesan A. S.	On the polarisation of light scattered by organic vapours.	Phil. Mag., **49**, *1216* (1925).
Krishnan K. S.	On the molecular scattering of light in liquids.	Phil. Mag., **50**, *697* (1925)
Ramanathan K. R.	The structure of benzene and cyclo-hexane and their optical anisotropy.	Nature, **116**, *279* (1925)
,,	The structure of molecules in relation to their optical anisotropy. Part I.	Proc. Roy. Soc., **107**, *684* (1925).
Raman C. V. and Ramdas L. A.	The scattering of light by liquid boundaries and its relation to surface tension. Part I.	Proc. Roy. Soc., **108**, *561* (1925).
,,	,, Parts II and III.	Proc. Roy. Soc., **109**, *150* and *272* (1925).
Ramanathan K. R.	Transparency and colour of the sea.	Phys. Rev., **25**, *386* (1925)
Banerji D.	Scattering of light in mixtures of air and CO_2.	Phys. Rev., **26**, *495* (1925).
Ramanathan K. R. and Srinivasan N. G.	The polarisation of light scattered by some organic vapours.	Proc. Ind. Asoc. Cult. Sci., **9**, *203* (1926)
Krishnan K. S.	A discussion of the available data on light scattering in fluids.	Proc. Ind. Asoc. Cult. Sci., **9**, *251* (1926).
Ramdas L. A.	The scattering of light by sputtered metallic surfaces.	Proc. Ind. Asoc. Cult. Sci., **9**, *323* (1926)
Krishnan K. S.	Are gaseous molecules oriented in a magnetic field?	Ind. J. Phys., **1**, *35* (1926).

Mitra M. N.	The molecular scattering of light at the critical state.	Ind. J. Phys., **1**, *137* (1926).
Raman C. V.	The birefringence of crystalline carbonates, nitrates and sulphates.	Nature, **118**. *264* (1926).
Raman C. V. and Krishnan K. S.	The electrical polarity of molecules.	Nature, **118**, *302* (1926).
Ramanathan K. R.	Intensity and polarisation of sky light at sunrise and sun-set.	Nature, **118**, *337* (1926)
Ramanathan K. R.	The structure of molecules in relation to their optical anisotropy. Part II-Benzene and cyclohexane.	Proc. Roy. Soc., **110**, *123* (1926).
Sogani C. M.	On the optical properties of chromatic emulsions.	Phil. Mag., **1**. *321* (1926).
Ramdas L. A.	The scattering of light by gaseous mixtures at high pressures.	Phys. Rev., **28**, *1030* (1926).
,,	The scattering of light by liquid surfaces.	Ind. J. Phys., **1**, *199* (1927).
Venkateswaran S.	The molecular scattering of light in aqueous solutions. Part I.	Ind. J. Phys., **1**, *235* (1927).
Sogani C. M.	X-ray diffraction in liquids.	Ind. J. Phys., **1**, 357 (1927)
Venkateswaran S.	The molecular scattering of light in aqueous solutions. Part II.	Ind. J. Phys., **1**, *393* (1927).
Ramanathan K. R.	On fluctuations of dielectric constant in liquids and theories of molecular scattering of light.	Ind. J. Phys., **1**, *413* (1927).
Rao S. R.	The scattering of light by liquids at high temperatures.	Ind. J. Phys., **2**, *7* (1927).
Banerjee A. N.	Scattering of light by aromatic compounds.	Ind. J. Phys., **2**, *51* (1927).
Rao I. R.	Determination and discussion of light scattering data of 10 gases and 63 vapours of aromatic compounds.	Ind. J. Phys., **2**, *61* (1927).
Sogani C. M.	Further studies in X-ray liquid diffraction.	Ind. J. Phys., **2**, *97* (1927).
Raman C. V.	The scattering of light in amorphous solids.	Journ. Opt. Soc. Am. **15**, *185* (1927).
Raman C. V. and Rao I. R.	Magnetic double refraction.	Nature, **119**, *528* (1927).

Raman C. V. and Sogani C. M.	X-ray diffraction in liquids.	Nature, **119**, *601* (1927).
Raman C. V.	Optical behaviour of protein solutions.	Nature, **120**, *158* (1927).
Raman C. V. and Sogani C. M.	X-ray diffraction in liquids.	Nature, **120**, *514* (1927).
Raman C. V. and Krishnan K. S.	The Maxwell effect in liquids.	Nature, **120**, *726* (1927).
Raman C. V.	Thermal degeneration of X-ray haloes in liquids.	Nature, **120**, *770* (1927).
Raman C. V. and Krishnan K. S.	Magnetic double refraction in liquids. Part I. Benzene and its derivatives.	Proc. Roy. Soc., **113**, *511*, (1927).
Krishnan K. S. and Raman C. V.	The magnetic anisotropy of crystalline nitrates and carbonates.	Proc. Roy. Soc., **116**, *549*, (1927).
Raman C. V. and Krishnan K. S.	A theory of electric and magnetic birefringence in liquids.	Proc. Roy. Soc., **117**, *1* (1927).
Raman C. V. and Krishnan K. S.	Electric double refraction in relation to the polarity and optical anisotropy of molecules. Parts I and II.	Phil. Mag., **3**, *713* and *724* (1927).
Raman C. V.	The molecular scattering of light in binary liquid mixtures.	Phil. Mag., **4**, *447* (1927).
Raman C. V. and Krishnan K. S.	The constant of the magnetic birefringence of benzene.	Compt. Rend. **184**, *449* (1927).
Ramachandra Rao S.	Further studies on light scattering in liquids at high temperatures.	Ind. J. Phys., **2**, *179* (1928).
Ramakrishna Rao I.	The optical anisotropy of atoms and molecules.	Ind. J. Phys., **2**, *435* (1928).
Ramachandra Rao S.	Effect of molecular form and association on light scattering in liquids. Part I. Fatty acids and alcohols.	Ind. J. Phys., **3**, *1* (1928).
Ramachandra Rao S.	Effect of molecular form and association on light scattering in liquids. Part I. Some aromatics.	Ind. J. Phys., **3**. *21* (1921).
Raman C. V. and Krishnan K. S.	A theory of light scattering in liquids.	Phil. Mag., **5**, *498* (1928).
Raman C. V. and Krishnan K. S.	A theory of the optical and electrical properties of liquids.	Proc. Roy. Soc. **117**, *589* (1928).

Annual Report for 1929

The following report on the activities of the Indian Association for the Cultivation of Science during the year 1929 is respectfully submitted to the Committee of Management.

Part I

Report on Scientific Investigations.

1. The Raman Effect.
2. Studies in X-ray Diffraction.
3. Diamagnetism and Molecular Structure.
4. List of Papers published in 1929.

Part II

Administrative Report.

5. Our Research Workers.
6. Lecture Arrangements.
7. Laboratory Equipment.
8. Workshop.
9. Library and Reading Room.
10. Financial Statement.
11. Acknowledgments.
12. Accounts for 1929.

Part I

Report on Scientific Investigations.

1. *The Raman Effect.*

The report for 1928 contained an account of how the investigations on the scattering of light which had formed a special feature of the work of our laboratory led up to the discovery of a new optical phenomenon of great interest. Immediately following the publication of the discovery, its further investigation was taken up with enthusiasm both at Calcutta and at numerous centres of research throughout the world. The literature of the subject grew rapidly, and Dr. A. S. Ganesan very kindly undertook to compile a bibliography of it which was published as a special number of the Indian Journal of Physics in August, 1929. This contained some 160 titles of papers with an abstract of the results contained in each publication. Since then, the effect has continued to receive attention from eminent investigators, and the significance of the phenomenon as offering a convenient method of investigation into problems, both physical and chemical, concerning the structure of matter is being increasingly realised. At the date of the writing of this report, the literature of the Raman effect extends to some 350 items. It appeared necessary to survey the literature once again. This has been done by Mr. S. Bhagavantam who has collected and classified the literature and written an introductory essay giving a general account of the effect and setting out its significance to various branches of research. His survey of the subject with its appendices forms an annexure to this report. In view of its publication, it is not necessary here to deal in further detail with the subject. It should however, be recorded that in spite of the absence of Sir C. V. Raman from

Calcutta during a considerable part of the year and the departure of Mr. Krishnan to join his new appointment at the Dacca University, the laboratory of the Association continued to participate in the development of the new field of research. A very active and enthusiastic worker has been Mr. S. Venkateswaran whose rare devotion to science enables him to find time for research after fulfilling the exacting duties of his office at the Government Test House. Both by himself and in collaboration with Dr. Ganesan and Mr. S. Bhagavantam, he has investigated the effect in a large number of organic liquids chosen to represent well-defined classes of carbon compounds. The very valuable results obtained were embodied in a memoir published in the Indian Journal of Physics, and in sundry papers contributed to the scientific periodicals, a list of which appears below.

In recognition of the importance of his discovery, the Honorary Secretary of the Association has been the recipient of numerous honours during the year under report. The Italian Society of Sciences, Rome, conferred upon him the Matteucci Gold Medal which is awarded for "the most important physical discovery of the year." This was followed by the honour of the conferment of knighthood by the British Government. The Faraday Society of London organized a well-attended discussion on "Molecular Spectra and Molecular Structure" at Bristol in September, 1929, at which several papers on the Raman effect and related topics were presented. Sir C. V. Raman was invited to open the discussion of the subject at Bristol. Invitations to lecture were received by him from numerous quarters, amongst others from the following which were accepted, namely the Universities of London, Cambridge and Edinburgh in Great Britain, the Universities of Paris, Aachen and Freiburg on the Continent, and the Physical Societies of England, France, Belgium and Switzerland. The University of Freiburg gave him the honorary degree of "Doctor Philosophiae Naturalis" and he received the Honorary membership of the Physical Society on the occasion of his visit to Zurich.

2. *Studies in X-Ray Diffraction.*

X-ray investigations were actively pursued in the Laboratory in the year under report. In the previous year's report, it was mentioned that X-ray diffraction in solutions enables us to find out the exact distribution of the solute molecules in the solvent. For instance, in a dilute solution of cane sugar in water, there was not only the ring due to the water, but a corona at small angles to the primary beam due to randomly distributed sugar molecules, the extent of the corona giving us an indication of the approximate dimensions of the dissolved molecule. This method would hence prove very useful in cases where direct determination of molecular weights becomes a matter of considerable difficulty, for instance, in colloidal and semi-colloidal solutions. A study of three typical colloids, dextrin, gelatine and sodium oleate in aqueous solution was therefore undertaken by Mr. P. Krishnamurti.[1] In dilute solutions, the extent of the coronae gave molecular weights which agreed fairly with the values determined by other methods. One important difference was however noticed between the soap solutions and those of dextrin or gelatin. Even in dilute solutions, the former showed an inner ring in addition to the water ring, which was in approximately the same position as that of the solid. Dilute solutions of dextrin and gelatin gave only the coronae in addition to the water ring. This shows clearly that soap solutions contain mainly groups of simple molecules or micelles, so that the pattern is similar to that of the finely divided powder suspended as it were in water, whereas in the other cases the division is molecular, not micellar. These observations are entirely in agreement with those of McBain and his co-workers on soap solutions.[2]

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[1] Krishnamurti, Ind. J. Phys., 3, 307)1929).

Binary Liquid Mixtures.

In view of the above facts it was considered that a study of binary liquid mixtures especially where one of the constituents was water would be interesting. Aqueous solutions of various concentrations in which the other component was phenol, trimethyl carbinol, piperidine, pyridine, butyric acid, ethyl alcohol, glycerine and lactic acid respectively were examined.[3] It was found that Wyckoff's conclusion that the pattern for the mixture is a superposition of those due to the constituents was not valid, the more so when we are dealing with polar and unsymmetrical molecules. A very dilute solution showed a scattering at small angles just as in dilute sugar solutions. But in more concentrated solutions, the effects observed differ widely. With phenol, trimethyl carbinol and piperidine the rings due to the two components exist separately in the pattern for the mixture at approximately the same angles as in the pure liquids. On the other hand, with glycerine, ethyl alcohol and lactic acid, only one ring is observed, the water ring having contracted and the ring due to the other liquid having expanded. It will be seen that the first group of liquids shows an analogy to sodium oleate, and hence we have to postulate the existence of groups of molecules in their aqueous solutions. The difference in behaviour between the two classes of solutions is due mainly to the difference in attractive forces existing between similar and dissimilar molecules in the mixtures. If the forces due to the former predominate then there is greater likelihood of similar molecules occurring together and *vice versa.* A distinction between the two classes is also indicated by other properties, notably miscibility and light-scattering power.

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[2] McBain and Salmon, J. Amer. Chem. Soc., 42., 426 (1920).
[3] Krishnamurti, Ind. J. Phys., 3, 331 (1929).

Among non-aqueous systems, a mixture of methyl salicylate and O-nitro benzaldehyde give a pattern almost identical with that obtained for either liquid. But with cyclohexane and methyl salicylate where the two kinds of molecules are dissimilar a different pattern is given for the mixture. The cyclohexane ring expands, and considerable scattering is noticed both inside and outside the halo.

In order to understand the origin of the diffraction haloes in liquids a few simple cases, *viz.*, those of tetranitromethane, CCl_4 and hexamethylenetetramine were examined,[4] the first two liquids in benzene and cyclohexane and the last one in water. All of them are symmetrical molecules and they crystallise in the cubic system. Both CCl_4 and tetranitromethane gave a strong inner ring and a faint outer one; and in benzene or cyclohexane solution, the pattern showed a strong scattering at small angles, the ring due to the solvent and an outer ring in approximately the same position as in the pure liquid. Since this outer ring persisted even in dilute solutions where the molecules were distributed at random, it was attributed to the structure factor of the molecule, and it agreed in position with the value calculated from the size of the molecule. This observation is very interesting when we compare it with the diffraction by CCl_4 vapour where a ring in a similar position is obtained[5] showing thereby that it is due to intramolecular arrangement. The origin of the inner ring has also been considered and shown to be due to the spacing of the planes containing maximum number of molecules per unit area in the solid which persist also in the liquid state.

Dr. K. Banerji[6] studied liquid amalgams of potassium and sodium by the K_a rays of molybdenum. The alloys could be regarded as solutions of either metal in Na_2K. It was found that when the excess of either component over that corresponding to Na_2K was small, the pattern was quite similar to that of Na_2K. But when either metal was in excess, it gave a pattern corresponding more to that of the pure metal.

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[4] Krishnamurti, Ind. Jour. Phys., *3*, 507 (1929).

[5] Debye, Bewilogua and Ehrhardt. Phys. Z., *30*, 84 (1929).

[6] Banerji, Ind. J. Phys., *3*, 399 (1929).

X-ray diffraction of a series of twenty-one liquids belonging to the terpene series has been examined by Mr. V. I. Vaidyanathan,[7] who found changes in the X-ray patterns with differences in structure of the molecules. The terpenes examined could be divided into four main groups, *viz.*, long chain olefinic terpenes, cyclic terpenes with CO group, mono-and dicyclic hydrocarbon terpenes and sesquiterpenes. The liquids in each class have their peaks in approximately the same position, but there is a shift in spacing when passing from one class to another. Of the liquids examined, camphene had a peculiarly sharp halo, and pinene showed two equally prominent ones. The sesqui-terpenes showed a diffuse ring outside the principal halo, the inner ring being present in some cases and absent in others.

Influence of Temperature on X-ray Haloes.

A short account of the influence of temperature on X-ray liquid haloes was given in last year's report. This subject has now been studied in detail by Mr. Vaidyanathan[8] with special reference to liquids showing two haloes which are also highly polar. Camphene, mesitylene, acetic and butyric acids, ethyl alcohol have been studied at ordinary temperature and between 130°-150°C.

An increase in scattering at small angles, a contraction of the haloes and an increase in their diffuseness were observed in all cases. In addition to these effects, in the case of liquids with two haloes, with rise of temperature, the separation between the inner and outer one tends to be effaced and also the inner haloes become more diffuse than the outer ones. In the case of acetic and butyric acids and in ethyl alcohol which are known to be associated to different extents at different temperatures these effects are specially striking.

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[7] Vaidyanathan, Ind. J. Phys., 3, 371 (1929).

[8] Vaidyanathan, Ind. J. Phys., 3, 391 (1929).

The changes from the solid to the liquid state have been followed by the X-ray diffraction method in the case of a few resins by Mr. Krishnamurti.[9] It was found that the contraction of the halo with temperature was greatest during certain intervals of temperature which was different for different resins. A similar anomalous rate in other physical properties, *viz.*, thermal expansion, specific heat, etc., recorded by Samsoen[10] and by Parks and Huffman in the change from the glassy to the liquid states is thus also indicated by X-ray diffraction.

X-ray Study of Coal.

Till now, X-ray investigations on coal were limited to the determination of ash-content as measured by the absorption of a beam of X-rays passing through it. The examination of coal by the Debye-Scherrer method with monochromatic radiation was started for the first time by Mr C. Mahadevan[11] in this laboratory. The two important varieties of coal, *viz.*, vitrain and durain were examined. Both gave two rings in approximately the same position as those of graphite, but were broad and diffuse showing the colloidal nature of the particles. This was more pronounced in vitrain with increasing moisture content. Durain gives several rings which are shown to be only superpositions of vitrain and ash rings, supporting the ideas of

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[9] Krishnamurti, Ind. J. Phys., 4, 99 (1929).

[10] Samsoen, Ann. de. Phys., Tome IX, 35 (1927).

[11] Mahadevan, Ind. J. Phys., 4, 79 (1929).

Fermor[12] that durain belongs to a colloidal system of the suspensoid type where vitrain acts as the dispersion medium ash as disperse phase.

The alpha, beta and gamma products isolated from coal by means of pyridine extraction were also studied. They gave a strong inner ring and a weak outer one, both of which are attributed to the complex carbon molecule. The further interesting fact was also found that the substances extracted both from vitrain and durain by means of pyridine gave similar X-ray patterns. This remark applies also to the gamma or resinic products obtained in both cases.

3. *Diamagnetism and Molecular Structure.*

In the Annual Reports of 1926, 1927 and 1928, references have already appeared to the investigations carried on in the Laboratory of this Association on the diamagnetism of gases, the magnetic anisotropy of crystals and the magnetic birefringence in liquids. Important progress was made during the year under report in correlating these different fields of enquiry and in gaining new ground, and it may be useful to give a summary of the work accomplished so far.

The subject of diamagnetism in relation to molecular structure has been approached at Calcutta from a rather unusual standpoint in connection with the investigations on the scattering of light. Apart from its relation to the Raman effect, the scattering of light yields much information concerning the various properties of molecules. It is known that light scattered by fluids in a direction perpendicular to the incident beam by an isotropic molecule is not completely polarised, but shows a considerable imperfection of polarisation. This imperfection is produced by the optical anisotropy of molecules. Attempts have been made by Bragg and Ramanathan[13] to compute the optical anisotropy of various structures on the basis of an interaction theory. Connected intimately with this phenomenon, there are two others, *viz.*, electrical and magnetic anisotropy associated with individual molecules. Such molecules, when arranged in the orderly manner which exists in a crystal lattice, present a state which displays a resultant degree of optical electrical and magnetic anisotropy depending on the manner of arrangement. Investigations on light scattering show that organic molecules, particularly those of the aromatic class, offer an interesting field of work from the above points of view in that the results obtained with the parent substance benzene indicate a high degree of anisotropy for the molecule.

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[12] Fermor, Rec. Geol. Sur. Ind., **60**, 347 (1928).

The relation between the crystal structure and the magnetic properties, especially in certain simple cases such as some nitrates and carbonates, has been fully discussed in a paper by Raman and Krishnan.[14] The observed magnetic anisotropy was quantitatively accounted for by taking into account the electronic structures of the nitrate and the carbonate ions. On the other hand very little work has been done with organic compounds. The same authors [15] have shown how the phenomenon of magnetic birefringence exhibited by liquids in a magnetic field can be utilised to determine the degree of magnetic anisotropy of the molecules concerned. In this way they proved that the benzene molecule has a high degree of magnetic anisotropy, the susceptibility in a direction perpendicular to the benzene ring being about twice as great as that in any direction parallel to the ring.

It was felt however that data for organic substances were lacking and a detailed investigation of their magnetic and optical properties was necessary. In two preliminary notes to Nature Sir C. V. Raman [16] has pointed out the importance of such investigations and the essential relationship between diamagnetism and crystal structure with special reference to organic crystals. The work was undertaken by Mr. Bhagvantam whose results were published in a series of papers during the year under report. [17] The main points will be briefly mentioned here.

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[13] Proc. Roy. Soc., Vol. 110, p. 123 (1926).

[14] Proc. Roy. Soc., Vol. 117, p. 1 (1929).

[15] Proc. Roy. Soc., Vol. 113, p. 511 (1927).

From analogy with benzene, the molecules of naphthalene, anthracene, etc., which contain two and three benzene rings respectively can be expected to display a prominent anisotropy. This has been fully confirmed by experimentation. The maximum magnetic susceptibility and the minimum optical polarisability are along a direction perpendicular to the plane of the benzene rings. Further it is found that the crystals of aromatic substances are generally highly anisotropic as against the aliphatic ones which display a comparatively feeble anisotropy. Sometimes the expected anisotropy is much greater than the actually observed value and in such cases the crystal structure is obviously more complex and the molecules are so marshalled that the effective anisotropy is decreased. The organic crystals can be divided into two divisions, one in which the directions of maximum optical polarisability and the minimum diamagnetic susceptibility very nearly coincide and the other in which they are crossed. The former are generally to be found in the aromatic and the latter in the aliphatic classes of compounds.

In this connection an important discovery of Cotton and Mouton, that certain liquids exhibit birefringence in a strong magnetic field, is of interest. The generally accepted explanation of the phenomenon is that the molecules, which

[16] Nature, Vol. 123, p. 494 (1929); Vol. 123, p. 605 (1929).

[17] Ind. Jour. Phys., Vol. 4, p. 1 (1929).

are optically and magnetically anisotropic are oriented in a magnetic field and the liquid as a whole exhibits birefringence. This effect depends on the magnitudes of the optical and the magnetic anistropies of the molecules concerned and its sign can be shown to depend on the mutual orientation of the principal magnetic and the optic axes. As mentioned before, it was shown by Raman and Krishnan that this phenomenon, supplemented by the observations on the scattering of light, can be utilised in calculating the magnetic anisotropy of the molecules. On the other hand, a direct measurement of the optical and magnetic anisotropies of crystals as was done by Mr. Bhagavantam[18] [10] affords a means of calculating the molecular anisotropies, if the crystal structures are known. With a view to correlate all these phenomena, extensive researches on the magnetic birefringence of various liquids and some solutions were undertaken by Mr. Ramanadham.[20] Making use of a powerful electromagnet constructed in this laboratory he was able to detect for the first time and measure the feeble birefringence exhibited by numerous aliphatic liquids. It was found that saturated aliphatic compounds usually show a feeble negative effect whereas the aromatic ones show a strong positive effect. From theoretical considerations it can be shown that the implications of such a result are that in the former class of compounds the direction of maximum optical susceptibility coincides with that of the maximum magnetic susceptibility whereas in the latter they are crossed. It is interesting to note that precisely the same conclusions have been arrived at by Mr. Bhagavantam from his investigations with crystals constituted by similar molecules. Mr. Ramanadham[21] has also deduced interesting relationships by discussing the significance of his results from the view point of chemical constitution.

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[18] Proc. Roy. Soc., Vol.124, p. 545 (1929).

[19] ,, Vol. 126, p. 143 (1929).

[20] Ind. Jour. Phys., Vol. 4, p. 14 (1929).

[21] ,, Vol. 4, p. 109 (1929).

From a comprehensive survey of all the above properties, Sir C. V. Raman was led to formulate a theory for the origin of colour in organic molecules.[22] It appears that colour is always accompanied by a high degree of asymmetry in the physical properties of the molecule resulting in a strong magnetic, optical and electrical anisotropies. A detailed account of the theory is given in a paper published in the Indian Journal of Physics.

4. *List of Papers published during the year 1929.*

INDIAN JOURNAL OF PHYSICS.

VOL. III, PART 3.

(1) On the Nature of Dextrin, Gelatin and Sodium Oleate Solutions as revealed by X-Ray Diffraction—By P. Krishnamurti.

(2) X-Ray Diffraction in Liquid Mixtures—By P. Krishnamurti.

(3) A Classical Derivation of the Compton Effect—By Prof. C. V. Raman

(4) X-Ray Diffraction in Liquids of the Terpene Series.—By V. I. Vaidyanathan.

(5) Influence of Temperature on the X-Ray Liquid Haloes—By V. I. Vaidyanathan.

(6) X-Ray Diffraction in Liquid Alloys of Sodium and Potassium—By Kedareswar Banerjee.

(7) The Kerr Effect in Viscous Liquids due to Radio-Frequency Oscillating Field—By S. C. Sircar.

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[22] Nature, *loc. cit.*

INDIAN JOURNAL OF PHYSICS.

VOL. III, PART 4.

(8) X-Ray Diffraction in Solutions and Liquids and the Molecular Structure Factor—By P. Krishnamurti.

INDIAN JOURNAL OF PHYSICS,

VOL. IV, PART 1.

(9) Magnetic Behaviour of some Organic Crystals—By S. Bhagavantam.

(10) Magnetic Birefringence in Liquids of the Aliphatic Series—By M. Ramanadham.

(11) The Relation between Colour and Molecular Structure in Organic Compounds—By Sir C. V. Raman and S. Bhagavantam.

INDIAN JOURNAL OF PHYSICS.

VOL. IV, PART 2.

(12) X-Ray Study of Vitrain and Durain and their Constituents—By C. Mahadevan.

(13) X-Ray Diffraction by Amorphous Solids—By P. Krishnamurti.

(14) Magnetic Birefringence in Solutions and its Relation to Crystal Structure and Properties—By M. Ramanadham.

INDIAN JOURNAL OF PHYSICS.

VOL. IV, PART 3.

(15) A Memoir on the Raman Effect in Liquids—By A. S. Ganesan and S. Venkateswaran.

INDIAN JOURNAL OF PHYSICS.

VOL. IV, PART 4.

(16) Bibliography of 150 papers on the Raman Effect-By A. S. Ganesan.

Philosophical Magazine.

(17) The Theory of Light-Scattering in Liquids.—By Prof. C. V. Raman.

(18) The Raman Effect in some Organic Liquids—By S. Venkateswaran.

Proceedings of the Royal Society of London.

(19) The Production of New Radiations by Light Scattering. Part I—By C. V. Raman and K. S. Krishnan.

(20) The Magnetic Anisotropy of Naphthalene Crystals.—By S. Bhagavantam.

(21) Magnetic and Optical Properties of Benzene Ring in Aromatic Compounds—By S. Bhagavantam.

Nature.

(22) Colour and Optical Anistropy of Organic Compounds By C. V. Raman.

(23) Diamagnetism and Crystal Structure—By Sir C. V. Raman.

(24) Investigations of Scattering of Light—By Sir C. V. Raman.

(25) Magnetic Behaviour of Organic Crystals—By C. V. Raman.

(26) A New X-Ray Effect—By Sir C. V. Raman and P. Krishnamurti.

(27) The Raman Effect in Carbon-disulphide—By A. S. Ganesan and S. Venkateswaran.

(28) Anomalous Diamagnetism—By Sir C. V. Raman.

Transactions of the Faraday Society.

(29) Investigation of Molecular Structure by Light Scattering—By Prof. Sir C. V. Raman.

Proceedings of Institute of Chemists (India).

(30) Constitution of Coal—By C. Mahadevan.

(31) Raman Effect and Chemical Constitution—By S. Venkateswaran.

(32) Structure of Organic Crystals—By S. Bhagavantam.

Economic Geology (University of Illinois).

(33) Chromite Deposits of Singhbhum—By C. Mahadevan.

Quart. Jour. of Min. and Met. Soc., India.

(34) Geological Traverse in South Singhbhum—By C. Mahavedan.

Part II

Administrative Report.

5. *Our Research Workers.*

Facilities for research work in our Laboratory were given during the year 1929 to 32 research workers belonging to different provinces. The Universities of Nagpur and Madras have each deputed a research scholar at their expense to work in the Laboratory of the Association.

6. *Lecture Arrangements.*

Regular courses of lectures in Physics and Chemistry for the benefit of students were delivered at the Association with the aid of our apparatus and demonstrators.

7. *Laboratory Equipment.*

Through the kindness of Mr. G. D. Birla and Mr. Sajan Kumar Chowdhuri, who each gave a donation of Rs. 1,500, one large Hilger El. quartz spectrograph was purchased. For this most valuable addition to our equipment, our best thanks are due to these gentlemen.

In addition to the above, the following instruments were purchased for the laboratory :

(1) 3 Quartz mercury arc lamps.
(2) 1 Small pumping outfit.
(3) 1 Cenco hyvac pump.
(4) 1 Weston milliameter.
(5) 1 Table fan.
(6) 1 1000 c.p. Pointolite lamp.

8. *Workshop.*

The following apparatus was manufactured during the year by the mechanics in the workshop of the Association :

(1) 3 Pairs round pole pieces for magnet.
(2) 1 Quartz thread holder.
(3) 2 Curie balances.
(4) 4 Holders for mercury lamp (from galvanised sheet).
(5) 2 Holders for bent glass compensator.
(6) 2 Holders for compressed glass compensator.

(7) 2 Holders with graduated circles for half shade compensator.
(8) 1 Holder for compressed glass compensator for use with half shade arrangement.
(9) 1 Pair of big pole pieces for electromagnet.
(10) Ball and socket brass joint with cylindrical adjustable stand.
(11) 2 Ice cameras.
(12) 2 Stands for glass tubes.
(13) 1 Brass camera. for x-ray.
(14) 6 Lead camera. for x-ray.
(15) One copper plate and one bismuth plate for Hall effect work.
(16) One brass vacuum camera for cathode-rays.
(17) 1 Holder for thin film. ,,
(18) Cathode end of sputtering apparatus.
(19) 2 Iron slits (from rod).
(20) Aluminum anticathode for cathode-ray tube.
(21) 4 Helmholtz coils.
(22) 2 Magnet field coils wiring.
(23) Torsion head with horizontal quartz fibre and graduated disc.
(24) Stand with pointed end on a base for rotating small crystals.
(25) 7 Glass cells in brass frame.
(26) One pair magnet pole pieces.

9. *Library and Reading Room.*

The following publications were subscribed for as usual :—

1. Scientific American.
2. Nature.
3. Science Abstracts, A and B.

4. American Journal of Science.
5. Philosophical Magazine.
6. Astrophysical Journal.
7. Chemical News.
8. Proceedings of the Royal Society, A.
9. Proceedings of the Royal Institution of Great Britain.
10. Transactions of the Royal Society, A.
11. Physical Review.
12. Physikalische Berichte.
13. Zeitschrift fur Physik.
14. Annalen der Physik.
15. Physikalische Zeitschrift.
16. Journal of the American Chemical Society.
17. Journal of Physical Chemistry.
18. Proceedings of the National Academy of Sciences, Washington.
19. Zeitschrift fur Kristallographie.
20. Zeitschrift fur Physikalische-chemie.
21. Annales de Physique.
22. Comptes Rendus.
23. Chemical Abstracts.
24. Revue de Optique.
25. Science Progress.
26. Naturwissenschaften.

We have to acknowledge with thanks the presentation of journals and periodicals in exchange of our Proceedings from the following societies and institutions :—

1. The Smithsonian Institution.
2. Cambridge Philosophical Society.
3. Physico-Mathematical Society, Tokyo, Japan.
4. Manchester Literary and Philosophical Society.
5. American Philosophical Society.
6. University of Illinois.
7. Akademie der Wissenschaften, Leipzig.

8. Franklin Institute.
9. South African Association for the Advancement of Science.
10. The Prussian Academy of Science, Berlin, Germany.
11. University of Philadelphia.
12. The Physical Society of France.
13. Bureau of Standards.
14. University of Iowa.
15. University of Calcutta.
16. Calcutta Mathematical Society.
17. Indian Chemical Society.
18. Reale Academia Nazionale Dei Lincei, Rome.
19. Societe de Physique et D' Historie-Naturelle, Geneva.
20. Journal of the Chemical Society, London and British Chemical Abstracts, presentation from Rai Bahadur Chunilal Bose.
21. Bayerischen Akademie der Wissenschaften, Munchen.
22. Der Gesselschaft de Wissenschaften, Gottingen.
23. University of Allahabad.
24. Imperial Agricultural Institute, Pusa.
25. Asiatic Society of Bengal.
26. Indian Institute of Science, Bangalore.
27. The Geological Survey of India.
28. Indian Mathematical Society, Journal presented by Sir C. V. Raman.
29. Academy of Sciences, Cracow.
30. University de la Brüno.
31. University of Brazil.
32. Academy of Sciences, Leningrad, Russia.
33. University of Durham.
34. Royal Academy of Sciences, Amsterdam.
35. Imperial Academy, Tokyo, Japan.
36. De la Facultad de Sciences, La Plata.
37. Royal Mateorological Society, London.
38. University of Frankfurt-a-Main.

39. Royal Dublin Society.
40. Tohoku Imperial University.
41. Institute of Physical and Chemical Research, Japan.
42. Royal Academy of Sciences, Copenhagen.
43. Kodaikanal Observatory.
44. College of Science, Kyoto, Japan.
45. National Research Council, Japan.
46. Academy of Sciences, Vienna, Austria.
47. Proceedings of the Royal Society of London, B. presentation from Sir C. V. Raman.
48. Transactions of the Royal Society, B. presentation from Sir C. V. Raman.
49. Societe Chimique, Zagreb, Yougoslave.
50. Hungary University (Szeged).
51. Ungarische Akademie, Budapest.
52. American Chemical Society.
53. Della Societa Italiana Di Fisica.
54. Societe De Chimie-Physique, Paris.
55. Mathematikai es Physikai Akademia, Budapest.
56. National Physical Laboratory of London.
57. Nederlandsch Tijdschrift Voor Naturkunde.
58. Comite de Reveu generale des Sciences.
60. Editor of " Physique Theorique."
61. University of Upsala.
62. University of California.
63. Wissenschaftlische Veroffentlichungen aus dem Siemens-Konzern.
64. Societe Polanaise de Physique, Warszawa.
65. Societe Vaudoise des Sciences Naturelles-Lausanne.
66. United States Department of Agriculture.
67. The Editor of Terrestrial Magnetism and Atmospheric Electricity.

10. *Financial Statement.*

On the 31st December, 1929, the Association had in the custody of the Imperial Bank of India Government Securities to the nominal value of Rs. 1,87,800 in the General Fund, Rs. 17,000 in the Ripon Professorship Fund, Rs. 1,000 in the Victoria Professorship Fund, Rs. 21,500 in the Maharaja Cooch-Behar Professorship Fund, Rs. 1,000 in the Hare Professorship Fund, Rs. 500 in the Nikunja-Garabini Prize Fund, Rs. 600 in the Jatindrachandra Prize Fund, Rs. 3,000 in the Dr. Sircar Research Medal Fund, Rs. 9,000 in the Joy Kissen Medal Fund, a floating balance in the Bank of Rs. 3,787-3-11 and a cash balance in the office of Rs. 937-13-6.

On the 31st December, 1928, the Association had in the custody of the Imperial Bank of India Government Securities to the nominal value of Rs. 1,87,800, in the General Fund. Rs. 17,000 in the Ripon Professorship Fund, Rs. 1,000 in the Victoria Professorship Fund, Rs. 21,500 in the Maharaja Cooch-Behar Professorship Fund, Rs. 1,000 in the Hare Professorship Fund, Rs. 500 in the Nikunja-Garabini Prize Fund, Rs. 600 in the Jatindrachandra Prize Fund, Rs. 500 in the Woodburn Medal Fund, Rs. 3,000 in the Dr. Sircar Research Medal Fund, Rs. 9,000 in the Joy Kissen Medal Fund, a floating balance in the Bank of Rs. 496-2-5 and a cash balance in the office of Rs. 124-12-9.

A copy of our balance sheet and the statement of Receipts and Expenditure during the year is attached to the Report.

11. *Acknowledgments.*

The thanks of the Association are due to the Honorary Engineers Rai Krishnachandra Banerjee Bahadur, and Babu Bhabadev Chatterjee, the Honorary Legal Advisers, Babu Jatindranath Basu and BabuNirmalchandra Chunder, to the Honorary Secretary, Sir Venkata Raman and to the Honorary Assistant Secretaries Babu Jyotishchandra Pal and Babu Ashutosh Dey, for their gratuitous services. The best thanks of the Association are also due to Mr. R. Ramjee Das Iyer for the generous donation of Rs. 5,000 made by him to the Funds of the Association in honour of the memory of his father, the late Mr. N. R. Iyer.

12. *Statement of Accounts for 1929.*

RECEIPT AND PAYMENT ACCOUNTS FOR

RECEIPTS.

	Rs.	As.	P.
Subscriptions	248	0	0
Donations	9,675	4	0
Rent from shops	4,332	0	0
Miscellaneous Receipts	3,295	8	9
Dr. Sircar Memorial Fund	405	0	0
Building Fund	250	0	0
Government of India Grant	20,000	0	0
Sale of Bulletins, etc.	3,121	15	6
Interest a/c. General Fund	6,543	6	0
„ „ Ripon P. Fund	575	0	0
„ „ N. G. Prize Fund	17	8	0
„ „ Jatindrachandra Prize Fund	21	0	0
„ „ Woodburn Medal Fund	17	8	0
„ „ Dr. Sircar Research Medal Fund	105	0	0
„ „ Victoria Prof. Fund	35	0	0
„ „ Maharaja of Cooch-Behar Prof. Fund	752	8	0
„ „ Hare Prof. Fund	35	0	0
„ „ Joykissen Medal Fund	315	0	0
Suspense Account	72	0	0
Provident Fund	574	3	0
Old Material sale	215	0	0
P. O. Savings Bank—withdrawn	140	0	0
Opening Balance on 1st January, 1929: Bank	496	2	5
Office	124	12	9
Rs.	51,366	12	5

Examined and found correct.

SAHA AND MAJUMDER,
Government Certified Auditors.

THE YEAR ENDED 31ST DECEMBER, 1929

PAYMENTS.

	RS.	AS.	P.
Commission a/c. General Fund	24	9	0
„ „ Ripon Prof. Fund ...	1	6	0
„ „ Nikunja G. P. Fund ...	0	3	0
Establishment Account	5836	2	0
Municipal Tax	1504	9	6
Electric Charges	1728	8	9
Gas Charges	510	13	9
Building Repairs	157	5	9
Furniture Account	1366	11	9
Laboratory Charges	6034	5	3
Workshop Charges	1469	1	0
Postage and Telegrams	1536	14	6
Printing Charges	4294	12	0
Miscellaneous Charges	4995	5	9
Telephone Charges	272	2	0
Research Scholarships	3675	0	0
Institute contribution to Prov. Fund ...	131	6	0
Scientific Instrument Account G. Fund ...	6385	14	3
Library Account	2968	2	0
Electric Installation Account	111	0	0
Electric Accessories	1763	13	9
P. O. Savings Bank Deposits	281	9	0
Suspense Account	142	0	0
Provident Fund	1450	0	0
Closing Balance on 31st December, 1929 :			
At Imperial Bank ...	3787	3	11
At Office	937	13	6
Rs.	51,366	12	5

C. V. RAMAN,

Honorary Secretary.

BALANCE SHEET

LIABILITIES.

	Rs.	As.	P.
General Fund	2,36,090	15	6
Investment Reserve Fund	77,808	0	0
Depreciation Reserve Fund *Property* ...	48,686	6	3
„ „ „ *Instruments* ...	49,307	7	8
„ „ „ *Furniture* ...	4,123	0	0
„ „ „ *Library* ...	15,892	12	4
Provident Fund	1,829	5	7
Victoria Prof. Fund	1,000	0	0
Ripon Prof. Fund	17,000	0	0
Maharaja of Cooch-Behar P. Fund ...	21,500	0	0
Hare Professorship Fund	1,000	0	0
Nikunja-Garabini Prize Fund	5,00	0	0
Jatindrachandra P. Fund	6,00	0	0
Joykissen Medal Fund	9,000	0	0
Woodburn „ „	5,00	0	0
Dr. Sircar Research Medal Fund ...	3,000	0	0
Dr. Sircar Memorial Fund	14,945	12	3
Vizianagram Fund	40	0	0
Building Fund	7,080	0	0
Dr. Sircar Research Medal Fund, Interest ...	840	0	0
Ripon Prof. Fund, Interest	1,638	6	3
Nikunja-Garabini Fund, Interest ...	300	0	2
Woodburn Medal Fund, Interest ...	211	8	0
Jatindrachandra P. Fund, Interest ...	165	11	0
Joykissen Medal Fund, Interest	969	0	0
Victoria Prof. Fund, Interest	70	0	0
Maharaja of Cooch-Behar Prof. Fund, Interest	1,505	0	0
Hare Prof. Fund, Interest	70	0	0
Government of India Grant	1,107	12	9
Rs.	5,16,781	1	9

We have examined the above Balance-Sheet with the books and vouchers and found it correct.

SAHA AND MAJUMDER,
Government Certified Auditors.

As at 31st December, 1929

ASSETS.

	Rs.	As.	P.
Land and Old Building	31,680	11	9
Lecture Hall and Gallery	23,465	5	3
Vizianagram Laboratory	40,900	14	0
Observatory Room	3,320	9	9
Range of Shops (East)	2,516	10	9
Range of Shops (West)	2,308	5	0
Servant's Quarters	1,024	0	0
Durwan's Quarters	303	13	9
Scientific Instruments (K. K. Tagore Fund) ...	25,000	0	0
Scientific Instruments (General Fund) ...	75,033	5	5
Botanical Instruments	2,329	6	0
Workshop Instruments	9,861	5	9
Tools and Implements	203	3	3
Library Account	39,657	2	7
Furniture Account	12,189	6	9
Suspense Account	77	9	0
Government Securities—3½ per cent. G. Fund	1,87,800	0	0
,, ,, Ripon Prof. Fund ...	13,000	0	0
,, ,, Victoria P. Fund ...	1,000	0	0
,, ,, Maharajah of Cooch-Behar P. Fund ...	21,500	0	0
,, ,, Hare P. Fund ...	1,000	0	0
,, ,, N. G. P. Fund ...	500	0	0
,, ,, Jotindrachandra P. Fund	600	0	0
,, ,, Woodburn M. F. ...	500	0	0
,, ,, Dr. Sircar R. M. F. ...	3,000	0	0
,, ,, Joykissen M. F. ...	9,000	0	0
,, ,, R. P. Fund 3 per cent.	4,000	0	0
Balance at P. O. Savings Bank	284	3	4
Imperial Bank	3,787	3	11
Office	937	13	6
Rs.	5,16,781	1	9

C. V. RAMAN,
Honorary Secretary.

20

On the Laue Photographs of Iridescent Crystals of Potassium Chlorate.

By

S. C. SIRKAR, M.Sc.

(Plate XI)

ABSTRACT.

The Laue pattern obtained by passing X-rays normal to the 001 face of a single crystal of potassium chlorate is compared with that produced under the same conditions, by the same crystal, heated almost to its melting point and then cooled. It is observed that in the latter case, each of a particular group of spots is split up into two and sometimes into three. A coloured crystal of potassium chlorate as well as a thick twinned crystal gave Laue patterns exactly identical with that produced by the heated crystal. The indices of the planes giving rise to these spots have been determined and it has been shown that these double spots are produced by a twinned crystal and the triple spots owe their origin to twinned strata more than two in number, situated inside the crystal not exactly parallel to each other. A study of the Laue photographs thus shows that on heating a single crystal of potassium chlorate, twinned strata, almost parallel to each other, appear in it, and that these strata are also present in the coloured crystals. These investigations thus lend support to the theory put forward by the late Lord Rayleigh to explain the iridescence of these crystals.

Introduction.

It is well known that beautiful iridescent crystals are very often obtained when potassium chlorate is crystallised from solution. The nature of light reflected by these coloured crystals was first studied by Stokes.[1] A few months later Madan[2] observed that on heating a single crystal of potassium chlorate almost to its melting point and then cooling it, the reflecting power of the crystal increases enormously and that the intensity and polarisation of the reflected light in different azimuths are exactly the same as those of the light reflected from a coloured crystal. The late Lord Rayleigh next put forward his theory of reflection at a twin plane[3] and in a separate paper[4] explained the iridescence of these crystals as well as the enormous reflecting power of the heated crystals. He assumed that these phenomena are produced by reflection at a great number of parallel planes of twinning and countertwinning situated at regular intervals inside the crystals, the distance between the successive planes being of the order of wavelength of light. The present Lord Rayleigh[5] has examined the sections of these crystals under high power microscopes and using plane polarised light, has obtained microphotographs showing the presence of many twinned and countertwinned strata in both coloured and heated crystals. He has also shown that in some cases, especially in the case of a heated crystal, these strata are not exactly parallel to each other. The present work was undertaken to see whether X-ray investigation of these crystals helps us in any way to understand the phenomena mentioned above.

The Laue Photographs.

The crystal of potassium chlorate belongs to the monoclinic prismatic class with the ratio $a : b : c = \cdot 8331 : 1 : 1\cdot 2673$ and

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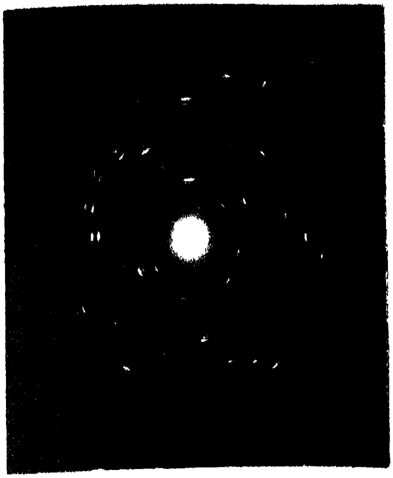
[1] Stokes, Proc. Roy. Soc., 38, p. 175 (1885).

[2] Madan, Nature, 84, p. 66 (1886).

[3] Lord Rayleigh, Phil. Mag., 26, pp. 251, 256 (1888).

[4] Lord Rayleigh, Proc. Roy. Inst., 12, p. 447 (1889).

[5] Lord Rayleigh, Proc. Roy. Soc. A, 102, 668 (1923).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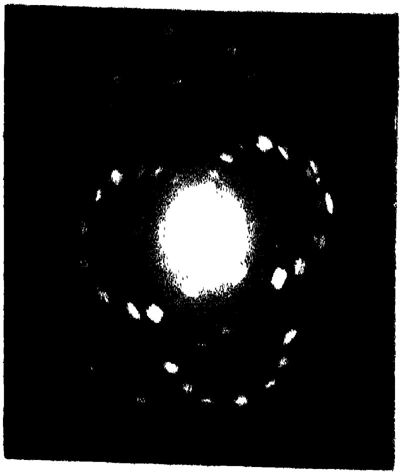
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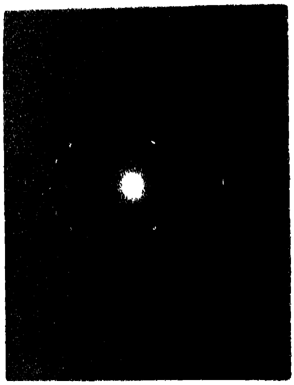
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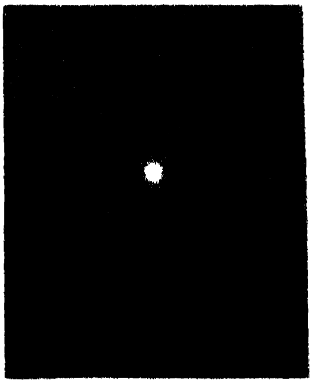
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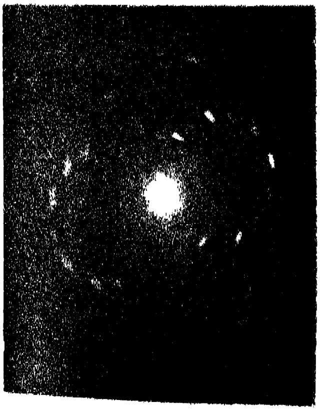
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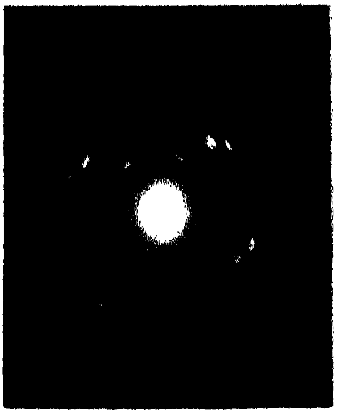
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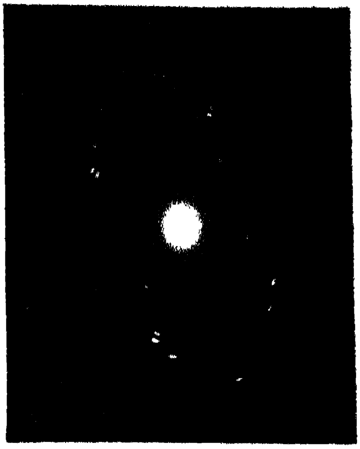
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the angle β equal to 109° 42′. Both iridescent and colourless crystals form rhombic or hexagonal plates parallel to 001 face. These crystals are very often twinned, the plane of twinning being parallel to the 001 plane. In taking the Laue photographs shown in Plate XI, X-rays were passed nearly normal to the 001 face. Figs. 1 and 2, Plate XI, show the Laue patterns due to a red and a bright green crystal respectively. Fig. 3, same plate shows the Laue pattern due to a thin single crystal of potassium chlorate. This crystal was heated almost to its melting point on a thick iron plate and when it cooled down, Laue pattern was again obtained. Fig. 4 is the pattern thus obtained. Fig. 5 is the pattern obtained by placing the heated crystal in such a way that the rays made a small angle with the normal to the 001 face. Figs. 6 and 7 show the patterns due to another thin crystal before and after heating. It will be noticed that each of a particular number of spots appearing as single in the case of the single crystal as shown in Fig. 3, is split up, sometimes into two and sometimes into three, in the case of coloured and heated crystals. The separation in a double spot is maximum for spots along *a* axis and minimum and practically absent in spots along *b* axis. The Laue pattern due to a thin twinned crystal was then obtained under similar conditions and is reproduced in Fig. 8, Plate XI. In this case also the spots referred to above appear as double. It is therefore natural to infer that twinned strata are present also in the coloured and heated crystals. In order to determine which planes give rise to these double spots, the indices of the planes were found out from a gnomonic projection. As the incident beam of X-rays was normal to 001 face and did not coincide with the direction of *c* axis of the crystal, the following method was adopted in determining the indices.

In Fig. 9, Z represents the crystal and ZO the direction of the incident beam perpendicular to the plane of the photographic plate XOY. Let the rays be

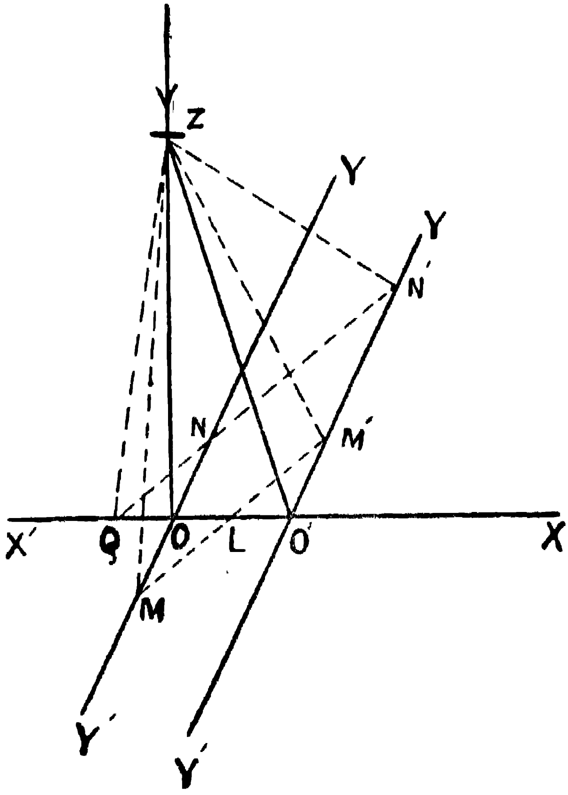

Fig. 9.

perpendicular to the 001 face of the crystal also, and the *a* and *b* axes of the crystal be parallel to OX and OY respectively. Then the *c* axis will be parallel to ZO′ making an angle β with OX. Let O′Z represent in magnitude and direction the *c* edge of the unit cell and let units be chosen on this scale along O′X and O′Y to represent *a* and *b* edges of the unit cell respectively. The point O at which the direct beam strikes the photographic plate represents the central spot. If now a gnomonic projection is obtained in the plane of the photographic plate, with the central spot O as origin, and with the same units in the directions OX and OY as along O′X and O′Y, the co-ordinates of the points on the projection will give the indices of the planes referred to the three axes OX, OY and

OZ. The inverse of the indices will give the intercepts along these axes. The actual intercepts on the three axes O′X, O′Y and O′Z of the crystal can now be found out easily from a knowledge of these intercepts. As for instance, if the intercept OL made by a plane ZLM on the axis OX be obtained from the indices h' k' l' of this plane referred to the axes OX, OY, OZ, the actual intercept O′L on the same axis is at once obtained, because it is equal to OO′ − OL where $OO' = c \cos(180^\circ\text{-}\beta)$. The true intercept O′M′ along O′Y is obtained from the similar triangles LO′M′ and LOM. When the true intercepts along the a, b and c axes are thus found, the true indices of the planes are easily obtained.

A gnomonic projection in the plane of the photographic plate was drawn for the pattern reproduced in Fig. 6. The distance OZ was 2·39 cms.; hence O′Z = 2·538 cms. If this length O′Z represent the c edge of the unit cell, the other two edges, a and b will be represented by 1·668 cms. and 2·003 cms. respectively. The distance OO′ is found to be 0·834 cm. and is thus equal to $\frac{a}{2}$ The indices of the planes giving rise to the double spots, referred to the axes OX, OY and OZ, were found to be $4k'1$ and $\bar{4}k'1$, where k' is either zero or any integer, positive or negative. Let ZLM represent a plane $4\bar{k}'1$. The intercepts measured from O along OX and OY are $\frac{a}{4}$ and $-\frac{b}{k'}$. Since $OO' = \frac{a}{2}$, the true intercept O′L $= -\frac{a}{4}$, and therefore L is the midpoint of OO′. Also, since the triangles LO′M′ and LOM are congruent, O′M′ = −OM. Hence the true indices of these planes are $\bar{4}k'1$. Similarly the true indices of the planes, having indices $4k'1$ referred to OX, OY, OZ are $\bar{4}\bar{k}'1$. Again the true intercept O′Q on the a axis made by the plane of apparent indices $\bar{4}k'1$ is equal to $-\frac{3a}{4}$. The true intercept O′N′ on b axis is obtained from the similar triangles QON and QO′N′

and is equal to $\frac{3b}{k'}$. Hence the true indices are $\bar{4}k'3$. Thus the true indices of the planes giving rise to double spots are $\bar{4}k1$ and $\bar{4}k3$, where k is either zero or an integer, positive or negative.

Explanation of the Origin of Double Spots.

A glance at Fig. 10 will make it clear how the double spots are produced in a Laue pattern due to a twinned crystal. Let the plane of twinning be perpendicular to the plane of the paper and let AB (Fig. 10) be the line of intersection of this plane with the plane of the paper. If OA represents the a axis in both the halves of the twinned crystal, the positive direction of c axis in the two halves will be parallel to OZ and OZ′. The b axis in the two halves will be perpendicular to the plane of the paper and it will be positive in the 1st half when the perpendicular is drawn upwards from the plane of the paper, and in the other half when it is drawn downwards. Let OZ represent the edge c of the unit cell and let OL and OQ represent $-\frac{a}{4}$ and $-\frac{3a}{4}$ respectively. Then ZL and Z′Q will represent the lines of intersection of the planes $\bar{4}k1$ and $\bar{4}k3$ with the plane of the paper. The structure of the single crystal of potassium chlorate has been completely determined by Zachariasen[1] and from a knowledge of the accurate values of the edges a, b and c of the unit cell, the angles ZLO and Z′QO can be determined accurately. These two angles are

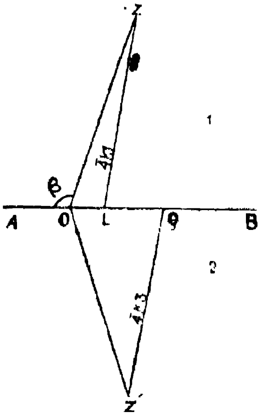

Fig. 10.

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[1] W. H. Zachariasen, Zeit. f. Cryst. 71, p. 501, 1929.

found to be equal to 100° 25′ and 80° 39′ respectively. Hence for any particular value of k, the plane $\bar{4}k1$ on one side of the twin plane and the plane $\bar{4}\bar{k}3$ on the other side make an angle of 1° 4′ with each other. Thus each of the planes $\bar{4}k1$ and $\bar{4}\bar{k}3$ in a twinned crystal will give rise to a double spot, the angular separation between the two spots being 2° 8′. It is actually found that the two constituents in every double spot in the case of all the patterns in which they appear, subtend an angle of about 2° 8′ at the crystal. If there be more than two twinned strata not exactly parallel to each other, each of the spots due to the planes $\bar{4}k1$ and $\bar{4}\bar{k}3$ will be spilt up into more than two. In the actual patterns obtained in the case of heated and coloured crystals, sometimes triple spots are obtained. Hence it is evident that in these crystals there are more than two twinned strata not exactly parallel to each other. These facts therefore corroborate the theory put forward by the late Lord Rayleigh[1] to explain these phenomena.

The author is indebted to Sir C. V. Raman, Kt., F.R.S., who kindly suggested the problem and under whose guidance the work was carried out.

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University College of Science,
Calcutta.

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[1] Lord Rayleigh, *loc. cit.*

21

X-Ray Study of Natural and Fossil Resins

BY

C. MAHADEVAN, M.A.

ABSTRACT.

Natural resins from widely separated areas and fossil resins of different geological ages were examined by the X-ray diffraction method. The patterns obtained with the two classes show no distinct difference. In all of them, a strong halo is present with the intensity maximum varying (according to the individual case) from 14½° to 16°—a striking feature about which is that the outer margin fades non-uniformly to haziness unlike the inner which is comparatively well defined. The patterns also show a great deal of general scattering between the direct spot and the inner margin of this halo.

A correlation of the variations noted in the intensity maxima of the resins with their well known physical characters brings out the fact that the softer resins give larger spacings and that with increasing hardness the intermolecular distances become smaller. The outer halo which is observed in some of the resins is shown to be due to incipient crystallisation of the products constituting the resins.

Two typical resins were broken up into resinic acids and resenes and studied by the X-ray diffraction method. They too give the intense halo within about the same range as that obtained for the untreated resins. The persistence of this feature in all the untreated resins and their products is surmised to be due to a structural similarity of the components in spite of the chemical variations ; most probably, they are related genetically to the cyclic hydrocarbon terpenes studied by Vaidyanathan.

1. *Introduction.*

The resins form a group of bodies of complex and variable chemical composition with more or less similar physical characters and occur in natural state as exudation from plants. In association with fossil woods and other organic mineral deposits of vegetable origin, often fossil resins are found in abundance. These fossil resins are also a useful product in industry and have been found to more or less answer the same needs as recent natural resins.

The resins have been variously classified by various workers [1]. Tschirch and Dieterich adopted the chemical affinity in their classification. In another classification, age factor is taken into consideration and they are thus divided into recent, recent fossil and fossil resins. This method is seen to be very unsatisfactory. Coffignier's [2] scheme of giving prominence to the physical factors such as hardness seems to be the most rational classification attempted so far. The hard resins have generally a higher melting point than the softer ones.

An X-ray examination of about twenty natural and fossil resins was carried out with a view to understand if these two groups showed any relationship and to see what light this evidence would throw on their physical characters and chemical constitution. Recent resins from widely separated areas and fossil resins of different geological horizons were obtained for the purpose. A study of turpentine was also made to facilitate the understanding of the observed phenomena.

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[1] For a full description, see 'Varnishes and their Components' pp. 109-110 by R. S. Morrell (Oxford Technical Publications) 1923.

[2] Nicolardot & Coffignier, Jour. Soc. Chem. Ind., Vol. 40, p. 310 A (1921).

2. *Results.*

On an examination of Tables I and II it is found that dammar, common congo, animi (Zanzibar copal), white gum dammar, brown kauri manilla, a fossil resin from Burma and another fossil resin—retinite-show a single intense halo, the inner side rather well defined but the outer very hazy with the intensity maxima lying between 14½° and 16°. On the other hand, hard manilla nubs, fine pale congo, kauri manilla, Sierra Leone copal (fine bold), white sambus, pale bush kauri, succinite, copalite, medium congo, spirit soluble manilla show two halos, one as intense as the halo noted in the first case with about the same spacing and the second halo between 38° and 41°. In both the cases, the space between the direct spot and the inner halo shows a good deal of general scattering. The resins studied may thus be divided into two groups—one showing a single halo and the other two halos. To understand the significance of such a classification in greater detail one typical resin from each of the two groups was broken up into resinic acids and resenes (Table III) and studied in detail. In the case of dammar fine bold (which gives only a single halo in the untreated state) it is seen that the acids obtained through extraction with 1% ammonium carbonate, 1% sodium carbonate, potassium hydroxide 1% and 0·1% give two distinct halos nearly in the same position as those obtained for the untreated two haloed resins. There is in addition evidence in these patterns of the presence of a third halo also, about midway between the two mentioned; its presence, however, is made out unambiguously in the resinic acids obtained from sodium carbonate extraction.

Hard manilla nubs (which gives two halos in the untreated state) was likewise broken into resinic acids and resenes. The X-ray patterns in this case are similar to those obtained for dammar with the difference that in the case of the resinic acids from potassium hydroxide, four halos are seen; they are sharper and better defined than in single haloed resins—much like a crystal powder pattern. The significance of this result is discussed in a later section.

Turpentine gives two halos, a very faint one at $a = 9{\cdot}96$ A. U. and a strong sharp halo at $a = 5{\cdot}75$ A. U.

Piauzite, an asphalt-like substance occuring in association with brown coals with a melting point of 315° shows a number of halos, one prominent and intense at 15° 14′ and the others rather faint at 17° 30′, 26° 23′ and 36° 52′.

3. *Discussion.*

In spite of the vast chemical researches[3] on resins, the nature of their constituents is little understood. The resins were formerly regarded as oxidation products of terpenes. While this was found to be true of some, it was contended that it may not be the general rule. According to the researches of Doebner, certain resins are known to be composed of the condensation products of aromatic aldehydes and phenols. Tschirch, from extensive researches classified the resins under the three heads, resin esters and their composition products, resinolic or resin acids and resenes. Resin esters yield on saponification aromatic acids such as benzoic and cinnamic acids. Resinolic acids are the characteristic free acids of resins and are in general, bodies of complex constitution and high molecular weight. To such a class belong the dammarolic acid $C_{56}H_{80}O_8$, dammarylic acid, $C_{86}H_{60}O_2$, trachylolic acid, $C_{56}H_{88}O_8$ and some monobasic, dibasic and oxyacids which have been isolated from several resins. Owing to the uncertainties and difficulties regarding the purity and analyses of the acids isolated, their exact chemical composition is little understood. The resenes which belong to the third group of substances existing in the resins are bodies about the nature of which little is known. Most of them may be the hydrates of terpenes (terpineol) though a few are stated to be derived from the oxidation of alcohols (resinols).

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[3] See R. S. Morrell, Varnishes and their Components, (*Loc. cit.*)

Köhler[4] suggests that the compound $C_{10}H_{16}O$ is the parent substance of resins which is converted to terpenes by the action of enzymes and to an acid by the action of oxygen and represents the equation thus

$$3C_{10}H_{16}O = \underbrace{C_{10}H_{16}}_{\text{terpene}} + \underbrace{C_{20}H_{30}O_2}_{\text{Acid}} + H_2O$$

The formation of a variety of resin acids is conceived by Grün[5] as being due to the condensation of pinene derivatives accompanied by the oxidation of one of the methyl groups to a carboxyl group. His structure for abietic acid supports such a conclusion besides explaining the occurrence of isomers of retene identified in some resins.

From the above brief resumé of the available chemical data regarding the resins, it is seen that no co-ordinated and widely accepted views exist regarding their nature or composition. It is interesting to examine the results obtained from X-ray study of resins in relation to the known facts regarding their chemical nature.

It is seen that all the resins, resin acids and resenes show an intense halo ranging, according to the individual case, from 5·5 A.U. to 6·3 A.U. with the inner edge of the halo rather well defined but the outer side fading non-uniformly to haziness. There is a great deal of general scattering between the direct spot (which is cut off by lead disc) and the intense halo.

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[4] John Köhler, J. Pr. Chem., Vol. 85, Pt. II, pp. 523-534 (1912).

[5] Ad. Grün, Zeits. Deut. Ol. Fett. Ind., Vol. 41, p. 49 (1921).

Since the terpenes and their related compounds have been identified in most resins, a comparison was made of the spacings obtained for the resins and their products with the results of Vaidyanathan[6] from his X-ray study of the terpene series. The correspondence of the spacings obtained in the resins by the author with those of the monocyclic and dicyclic hydrocarbon terpenes deduced by Vaidyanathan is striking. With a spacing of 5·44 A.U. for terpinene, his values go on gradually increasing to 6·02 A.U. for the pinenes—nearly the same range within which the spacings for the resins lie. This behaviour bears a close analogy to the phenomenon exhibited by several long chain compounds both in the liquid[7] and solid states[8] which, however, show a nearly constant spacing of about 4·8 A.U. characteristic of the aliphatic series. Sogani explained it as being due to the peculiar arrangement of the long molecules, the spacing corresponding to the thickness of the molecules, hence being independent of the length of the chain. From analogy it is to be concluded that the spacings 5·5 A.U.—6 A.U. (within which range all the resins examined lie) is characteristic of a class of constituents persisting in them all. In spite of differences in chemical composition, the above observations suggest that the resins and their products have a structure the geometry of which is similar to that of the group of terpenes just mentioned.

To understand this relationship more clearly, turpentine oil, a product genetically associated with rosin was examined by X-ray method; it gives two halos, the inner very faint with $a = 9{\cdot}96$ A.U. and the outer strong and well defined having a spacing of 5·75 A.U. On comparison with Vaidyanathan's[9] data, the correspondence of this value with the spacing for the pinenes is easily made out. In the light of the fact that turpentine oil consists predominently of pinenes, the above result is quite intelligible. The small discrepancy in the outer ring is easily explained when we remember that turpentine is not pure pinene but contains other terpenes as well.

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[6] V. I. Vaidyanathan, Ind. Jour. Phys., Vol. III, Pt. 3, pp. 371-389 (1929).

[7] C. M. Sogani, Ind. Jour. Phy., Vol. II, Part I, pp. 97-139 (1927).

[8] Muller and G. Shearer, Chem, Soc. Jour., 123, pp. 3156-3164 (1923).

The case of the acids obtained from the resins may next be considered. Here also, it is seen that the intense halo is between 5·5 A.U. and 6·3 A.U. The acid constituents possessing a high molecular weight such as dammarolic acid, trachylolic acid, abietic acid, etc., are likely to have a very complex structure, the nature of which is not clear from chemical evidence. They are said to consist in essence of a retene nucleus. Whereas it is not possible to understand precisely the way they manifest themselves in the X-ray pattern, it may be pointed out that the diffuseness of the outer margin of the strong halo—a feature observed in the resin acids as well as the resins—may be just due to this complexity of constitution of the resin acids. This inference finds further support from the fact that in comparatively simpler compounds of the resin class such as turpentine oil, the halos are equally well defined on the outer and inner margins.

In the products of saponification of the resins, in addition to the complex acids mentioned, benzoic, cinnamic and similar single nuclear aromatic acids have been identified. The esters of these acids are surmised to be present in the resins. Since the spacings for such compounds range between 5—5·5 A.U. they may be superposed on the patterns due to the other compounds constituting the resins.

The resenes too give a pattern much like the resins and resin acids; their relationship to terpenes from chemical evidence has already been alluded to. The spacings may be mainly due to the terpene derived compounds.

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[9] V. I. Vaidyanathan (*loc. cit.*), p. 378.

Finally the untreated resins themselves give spacings varying from 5·5 A.U. to 6·12 A.U. Since their constituents, *i.e.*, the acids, esters and resenes all give values within that range, it is natural to see the persistence of those spacings in the untreated resins themselves. It may be pointed out in conclusion that the space between the direct spot and the intense inner halo shows a great deal of uniform general scattering; as emphasized earlier, the outer edge of the halo fades non-uniformly to haziness.

A closer examination of these spacings shows that there are distinct but slight variations amongst the resins themselves. This may in part, as has been shown above, be attributed to the variations in the composition of the substances which though essentially of an aromatic nature have differently substituted compounds in the several resins.

In addition to this influence of such compositional variations, we have to take into account the physical state of the resins themselves. Correlating the physical data of the resins, it is seen that the softer resins (which have a lower melting point) give spacings that are larger than those obtained for the harder resins. Thus the dammars which are the softest in the group with a melting point between 80° and 100° have spacing of a little more than 6 A.U. The manillas and the kauris, less soft than the dammars (M.P. 120° to 160°) have a spacing of about 5·8 A.U. The congos with medium hardness (M.P. 160° to 180°) show a spacing of 5·7 A.U. The hard resins Sierra leone copal and Zanzibar copal (animi) give the minimum with a spacing of 5·5 to 5·6 A.U. It may be remarked here that similar changes in the spacings have been observed [10] in some resins in which softening was induced by rise in the temperature.

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[10] S. S. Ramasubramanyam, Ind. Jour. Phys., Vol. III, Pt. 1, p. 148 (1928). Also see P. Krishnamurti, Ind. Jour. Phys., Vol. IV, Pt. 2, pp. 99-108 (1929).

Besides the observation of the universal feature of the occurrence of an intense halo ascribable to the loaded aromatic ring, it is noted in some of the resins (Tables I and II) that a second larger halo of the order of a crystalline spacing (2·1 A.U. to 2·4 A.U.) is also present. An interpretation of the presence of this second ring was attempted by studying the X-ray pattern of the acids and resenes obtained by breaking up the resins. As described earlier, two typical cases, one from each group—dammar fine bold for the single haloed and hard manilla nubs for the double haloed resins—(the resins in which the resinic acids and resenes preponderate) were studied in detail. The acids obtained from both these resins show in all cases two halos distinctly; in addition, there is evidence of a third halo intermediate in position between them. In a few cases they are quite distinct. This suggests that under favourable conditions the resinic acids show a tendency towards crystallisation. The smaller spacing in the untreated two haloed resin is doubtless due to the existence of this incipient state of crystallisation. An additional proof of this inference is afforded by the fact that the hard manilla nubs shows a clear crystal powder pattern with four rings for one of its acids, which is what we should expect since this resin showed evidence of incipient crystallisation even in its untreated state. On the other hand the acids in the one haloed resin seem to be in a lower state of crystallisation. The above conclusions are in agreement with the independent observations of Naray Szabo[11] who attributes the smaller spaced halo to incipient crystallisation.

4. *Piauzite.*

Piauzite stands out exclusively in this group in that it gives four distinct halos unlike the other members described so far. The halo at about 6 A.U. which is present in all the resins persists here with the same intensity and is the most prominent of all the rings. This suggests an unmistakable relationship to the constitution of resins. The other three halos are faint but sharp and well defined. Piauzite is known to contain ash of about 6 per cent. The two halos 3·37 A.U., 2·44 A.U. are not dissimilar to the ash rings of coals. One more halo at 5 A.U. has to be accounted for. Calculations of spacings for the probable ash constituents were made from Hull's formula,[12] and for FeS_2 a spacing of 4·7 A.U. is obtained. It is probable that the halo in piauzite with $a=5$ A.U. is due to this source of mineral matter.

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[11] Stefan V. Naray Szabo, Bio. Chem. Zeit., Vol. 186, p. 86 (1927).

Thus these observations are in conformity with the fact that piauzite after melting burns with an aromatic odour emitting much smoke and the halos consist of one due to the resin together with three others ascribable to the associated mineral matter.

5. *Experimental.*

A Shearer tube with aluminium cathode and copper target was used as the source of X-rays. 'Cenco-hyvac' backing pump and Waran's mercury diffusion pumps maintained the vacuum in the tube and an oil cooled transformer supplied the high tension. The resins were ground to dimensions of about 1 m.m. thick and suitably mounted. An exposure of $3\frac{1}{2}$ hours was given for each sample with 6 mil-amps in the secondary circuit. The resulting diffraction pattern was received on an Isozenith photographic plate kept at a distance of about 2·6 cm. After deducing the diffracting angle, the intermolecular distances in the substance were calculated from the well known Bragg formula.

$$a=\frac{\lambda}{2\sin \theta/_2}$$

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[12] A. W. Hull, Phys. Rev., Vol. 10, p. 678 (1917).

For obtaining the resinic acids, Tschirch's[13] method was adopted. The resins were powdered and dissolved in ether; dammar was nearly soluble in ether whereas hard manilla nubs left more than 50 per cent. of insoluble matter. The solution of the resin in ether was extracted in succession with 1 per cent. ammonium carbonate, 1 per cent. sodium carbonate, 0·1 per cent. potassium hydroxide and 1 per cent. potassium hydroxide solutions. The extract in each case was acidulated with dilute hydrochloric acid, when the resinic acids were precipitated. The precipitate was washed and dried in a vaccum desiccator.

The non-extracted part of the ether solubles of the resin was subjected to steam distillation to remove the essential oils and the resenes were left behind after this treatment. All the products thus obtained were studied by the X-ray diffraction method.

The experiments were carried out in the laboratories of the Indian Association for the Cultivation of Science and the author is grateful to Sir C. V. Raman, Kt., F.R.S., for his helpful criticism and continued interest.

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[13] Allen. Commercial Organic Analysis, Vol. II, Pt. 3, p. 142 (J & A Churchill).

TABLE I

Recent Resins.

Name of Resins.	Intense θ_1	Faint θ_2	$a = \frac{\lambda}{2 \sin \theta_1/_2}$	$a = \frac{\lambda}{2 \sin \theta_2/_2}$	Hardness*	Melting point
White Gum Dammar	14°29′	...	6·12	...	23	90°
Dammar Fine Bold	14°39′	...	6·04	...	23	90°
Kauri Manilla	14°41′	37°59′	6·02	2·37	17-16	120°
Spirit Soluble Manilla	15°4′	38°24′	5·87	2·34	16-17	150°
Hard Manilla Nubs	15°14′	38°7′	5·81	2·36	16-17	150°
Brown Kauri Manilla	15°14′	...	5·81	...	16-17	150°
Pale Bush Kauri	15°14′	...	5·81	...	16	150°
White Sambus	15°40′	38°40′	5·65	2·33	16	160°
Common Congo	15°40′	...	5·65	...	13	180°
Medium Congo	15°40′	39°3′	5·65	...	13	180°
Fine Pale Congo	15°41′	38°16′	5·66	2·35	13	180°
Sierra Leone Copal	15°53′	38°24′	5·58	2·34	4	190°
Animi (Zanzibar)	16°4′	..	5·51	...	1	260°
Turpentine oil	9°1′	15°16′	9·96	5·75		
	Faint	Intense	Faint	Intense		

TABLE II

Fossil Resins.

Name of Resins.	Intense θ_1	Faint θ_2	$a = \frac{\lambda}{2 \sin \theta_1/_2}$	$a = \frac{\lambda}{2 \sin \theta_2/_2}$
Fossil Resin, Burma	14°39′	...	6·84	...
Retinite	15°14′	...	5·81	...
Succinite	15°39′	40°37′	5·71	2·22
Jaintia Fossil Resin	15°40′	41°38′	5·64	2·17
Palana Fossil Resin	15°41′	40°14′	5·66	2·24
Copalite	15°53′	41°38′	5·58	2·17

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* Bottler's scale of Hardness (see Natural & Synthetic Resins, R. S. Morrell p. 9, 1926).

TABLE III

Resinic Acids and Resenes.

Resin	Dammar Fine Bold			Hard Manilla Nubs.			
Reagents for extraction.	a_1	a_2	a_3	a_1	a_2	a_3	a_4
1% Ammonium Carbonate	6·20	3·21	2·26		***		
1% Sodium Carbonate	6·30*	3·19*	2·20*	5·50	3·19	...	2·33
0·1% Potassium Hydroxide	6·30	3·19	2·24	5·50	**	**	2·37
1% Potassium Hydroxide		***		6·04	3·41	2·62	2·32
Resenes	6·30		2·20	5·81	**	**	**

TABLE IV

Piauzite.

Number of the Halo.	Remarks.	θ	$a=\frac{\lambda}{2\sin\theta/_2}$	Origin.
1	Intense	15°14′	5·81	Resinous matter.
	Very fair	17°30′	5·06	Mineral matter.
3	Fair	26°23′	3·37	Mineral matter.
4	Fair	36°52′	2·44	Mineral matter.

* Very distinct. ** Indistinct. *** Very little acid obtained.

22

Precessions of an Elliptical Orbit.

(*Notes on : Vibrating Strings ; Planetary Orbits; The Raman Effect.*)

By

D. D. Kosambi.

I. Any text-book of hydrodynamics will give the following equations for the motion of an infinite cylinder through a perfect incompressible fluid, at rest at infinity :

$$(1) \qquad (M+M')\ddot{\xi}+k\rho\dot{\eta}=X$$

$$(M+M')\ddot{\eta}-k\rho\dot{\xi}=Y.$$

$$(2) \qquad (M+M')\ \frac{dU}{dt}=P$$

$$(M+M')\ U\frac{d\psi}{dt}=k\rho U+Q.$$

Here, **M** is the mass of an unit length of the cylinder, M' that of the fluid displaced thereby ; ξ, η coordinates of the central axis with respect to axes fixed in space, the whole motion being in a direction perpendicular to the length of the cylinder. The constant of circulation about the body is denoted by k ; density of the fluid medium by ρ ; components of the external force per unit length by X, Y. In equations (2), P, Q are components of the external force along the tangent and normal to the path of the center ; ψ the angle made by the direction of the velocity U, with a fixed direction. (*Cf.* Lamb, Hydrodynamics, 5th ed., p. 76.)

The important characteristic of these equations is that the total energy of the motion represented is exactly the same as when there is no circulation ($k=0$). In fact, the force of circulation is perpendicular to the velocity, and so does no work. These equations may be made also to represent the case of an electron in a magnetic field, a Foucault pendulum, and even the restricted problem of three bodies, as by the equations of Hill. We proceed to consider special cases.

II. If a vibrating string be set in motion by plucking it in the middle, most of its motion will be represented by—

$$y = A \sin bx \sin bct \tag{3}$$

Seen lengthwise, the string is approximately our infinite cylinder attracted to the center with a force proportional directly to the distance. Due to natural unevenness of the apparatus the actual path will be a flat ellipse rather than a straight line, and so circulation of the air will be set up. Our equations (1) become :

$$\left.\begin{aligned} \ddot{\xi} + 2\nu\dot{\eta} + \lambda^2\xi = 0 \\ \ddot{\eta} - 2\nu\dot{\xi} + \lambda^2\eta = 0 \end{aligned}\right\} \quad \nu = \frac{k\rho}{2(M+M')}, \quad \lambda^2 = \frac{\text{force at unit distance}}{(M+M')} \tag{4}$$

These may be formally integrated by an ingenious device due to Bromwich (Proceedings of the London Math. Soc. Series 2, Vol. XIII, p. 225). Multiplying the second by $i = \sqrt{-1}$ and adding to the first, we have :

$$\ddot{z} - 2\nu i z + \lambda^2 z = 0, \qquad z = \xi + i\eta, \quad i = \sqrt{-1} \tag{4a}$$

$$\text{whence} \qquad z = c^{\nu i t} \left(Ae^{ipt} + Be^{-ipt} \right) \tag{5}$$

$$\text{where} \quad p = \sqrt{\nu^2 + \lambda^2}$$

With the initial conditions $z'=0$, $z=a$, when $t=0$, the motion follows an hypocycloid tangent to $| z \quad \frac{a\nu}{r}$ with cusps on the circle $| z | = a$.

With another set of initial conditions, say $\xi_0=\eta_0=\dot{\eta}_0=0$ $\dot{\xi}_0=\nu$ when $t=0$ we obtain :

$$z=\frac{\nu}{p}e^{\nu it}\sin pt \tag{6}$$

In polar co-ordinates, $z=re^{i\theta}$

$$\theta=\nu t, \qquad r=\frac{\nu}{p}\sin pt \quad or \quad r=\frac{\nu}{p}\sin\frac{p\theta}{\nu} \tag{6a}$$

The path is thus a rosette, described by a casual observer as a rotating ellipse, as also in the gyroscopic pendulum. We see that a new period has appeared, that of precession :

$$T=2\frac{\pi}{\nu}=\frac{4\pi(M+M')}{k\rho} \tag{7}$$

Actually if one tightens the heavy string of a banjo, and plucks it in the middle, the whole motion seems a blurred region to naked eye, and its boundaries, instead of narrowing down uniformly to rest because of air resistance, are seen expanding again, after a little while. The period of this expansion would be just a half of the above. An ink dot on the string apparently follows the "rotating ellipse," and the period of a full rotation would then be T. An experiment seems to be called for with brilliant points and photographic observations.

III. The theory of relativity has still to account for the observed precessions of perihelion in our planets, especially Venus. We can consider the atmosphere of the planet and other light surrounding debris such as the rings of Saturn as constituting a circulatory effect with respect to the space occupied by the planet, since the rotation of the planet is sure to set this matter into motion. Unfortunately, the infinite cylinder cannot yield numerical results applicable to the planetary case, and the three-dimensional analysis presents difficulties. However, a criterion may be obtained as to the direction of rotation of the planet, *i.e.*, as to the circulation set up. Notice in passing that Venus is known to have a dense atmosphere though the question of its period of rotation about its axis is still a point of some doubt.

Instead of taking equations (1) with attraction inversely as the square of the distance, we assume the divergence from the normal state to be small and apply equations (2).

$$\text{(8) Let} \quad \left.\begin{array}{l} U = U_1 + U_2 \\ \psi = \psi_1 + \epsilon \end{array}\right\} U_1,\ \psi_1,\ \text{as in the Keplerian condition.}$$

$$\text{then} \quad (M+M')\frac{dU}{dt} = P = (M+M')\frac{dU_1}{dt} \quad \therefore \quad U_2 = 0$$

$$\text{and} \quad (M+M')U\frac{d\psi}{dt} = k\rho U + Q \ \text{ and } \ (M+M')U_1\frac{d\psi}{dt} = Q$$

$$\text{whence} \quad \frac{d\epsilon}{dt} = \frac{k\rho}{M+M'} \quad \text{and} \quad \epsilon = \int_0^t \frac{K\rho dt}{M+M'}$$

which leads to the result that ϵ in a complete period increases by $\frac{k\rho T}{M+M'}$. If the direction from which ψ is measured be taken as the radius vector to the perihelion, the orbit being nearly circular, the perihelion is retarded by this amount if k be positive. The actual direction of precession depends only on the direction of circulation. An advance would signify that the directions of circulation and of description of the orbit were opposite; a retardation would mean that they were identical. Finally, this precession when small might also be taken as a slight change of period of the moving body: advance of perihelion as an increase of period, retardation as a decrease. In the string, the circulation is set up by the vibration itself and a retardation should always occur.

IV. The solar system is but a step from the atomic model. The two-dimensional fluid motion of our cylinder, of a vortex, of an electric charge in an electromagnetic field are indistinguishable. Thus the change of period just pointed out in the case of a planet might well be seen as an extra line of the spectrum, if all the electrons have a sole direction in describing the orbit; as two lines, symmetrically displaced from the ordinary line, if the constituent electrons have both senses of description. And indeed, this is the usual explanation of the well known Zeeman effect, after Larmor. In the Raman effect, however, a number of electrons are excited by a light wave and send out a certain number of extra waves not yet satisfactorily explained (the Smekal jump is most unattractive). We might extend our analysis, and replace the constant of circulation k by a periodic function of the time which represents the change of electromagnetic intensity. The phenomenon and the problem will not be discussed in the present note, though I hope a suggestion will not be ill received. Quantisation and the critical value method of Schrödinger should be used to obtain the proper numbers corresponding to the new periods caused by the disturbing function. Secondly, the asymmetry of the Raman effect has also to be considered. The Zeeman effect might be observed, for purposes of comparison, in a magnetic field wherein the intensity has a period comparable to that of the light waves used in the more recent discovery. Let it finally be noticed that while electrodynamically unsound models have usually been employed for purposes of illustration and deduction, equations of our type will be applicable wherever a stable periodic motion of any given system is acted on by "non-energic" forces, here forces perpendicular to the displacement. As for the mathematical justification of the assumption that in an arbitrary system, a number of stable recurrent—if not periodic-motions exist, the reader is referred to modern dynamical theorists, such as Birkhoff.

HARVARD UNIVERSITY, SEPTEMBER, 1927.
BENARES HINDU UNIVERSITY, APRIL, 1930.

Note.—The Kármán solution involving rotational motion of the fluid about the infinite cylinder has been neglected ; it should most certainly be taken into account in any experiments with vibrating strings.

23

The Effect of Pressure on Absorption of Spectral Lines.

BY

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AND

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(*Received for publication, 15th May, 1930.*)

(Plate XII.)

1. *Introductory.*

On the theory of atomic structure due to Bohr and Sommerfeld, radiation or absorption is the result of transfer of the valence electron from one orbit to another. There are a certain number of orbits whose positions are fixed by the energy content of the electron. Assuming the orbit to be circular the radius is given by $\frac{h^2n^2}{4\pi^2 meE}$, here n is the total quantum number of the orbit and E the charge on the nucleus. For hydrogen this is ($\cdot 532 \times 10^{-8} \times n^2$ cm). If we have a number of atoms in an enclosure and if they are excited, the diameter of the farthest orbit of the valence electron that may be developed obviously cannot exceed the distance between two atoms or rather the distance of the mean sphere of action between the two atoms. If the atoms are excited by suitable incident radiation, frequencies above that corresponding to the development of the outermost orbit, undergo faint general absorption as in X-ray spectra.

This line of reasoning has been adopted by Dr. Saha in a letter in Nature,[1] to explain why different stars show different number of lines for the same element in the Fraunhofer spectrum. In the case of our sun for most of the elements the limit is about 6 lines. He postulates therefore that the pressure in the outer layers of the photosphere is such that the orbits beyond the sixth are rarely developed. Beyond this the atoms only exert a sort of cumulative continuous absorption. Hence among the Fraunhofer lines the longer wavelengths come from the interior while the higher frequencies come from the upper layers. Since the density (and the luminosity) of the concentric layers decreases rapidly we have 35 lines of hydrogen in the chromospheric radiation. The intensity of these 'Flash' lines is, however, about one-thousandth of the 'dark' lines of the Fraunhofer spectrum. The spectrum of Sirius shows 13 Balmer lines, while α Cygni where the pressure is much less shows 24 lines. Since n (of the highest orbit) varies as $\left(\frac{T}{P}\right)^{\frac{1}{6}}$, the fact that our sun shows only six lines is ascribed by Saha to a higher pressure and a lower temperature than in Sirius.

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[1] Nature, Aug. 2, 1924.

Practical evidence on these points is lacking. R. W. Wood[1] has shown that with a long tube in which probably the distance between the atoms is comparatively large photographs up to the 20th line may be obtained. In the case of absorption however such experiments have not yet been made. These experiments were therefore taken up to see how pressure affects the number of lines developed by the atoms of a vapour on which a continuous radiation falls, potassium being chosen for the purpose.

2. *Experimental.*

A suitable source of continuous radiation is the first thing of importance in the absorption experiments. The crater of an ordinary carbon arc does not show any continuous radiation beyond λ 3200, but as the limit of the principal series of potassium stretches as far as λ 2850 it was necessary to obtain a source capable of emitting a continuous radiation up to that limit. After a number of trials a soft carbon arc fed with uranium compound was found most suitable as it gave a practically continuous background stretching far into the ultra-violet.

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[1] Proc. Roy. Soc., 97, p. 455.

A quartz spectrograph (kindly lent by Sir C. V. Raman) was used for taking the photographs.

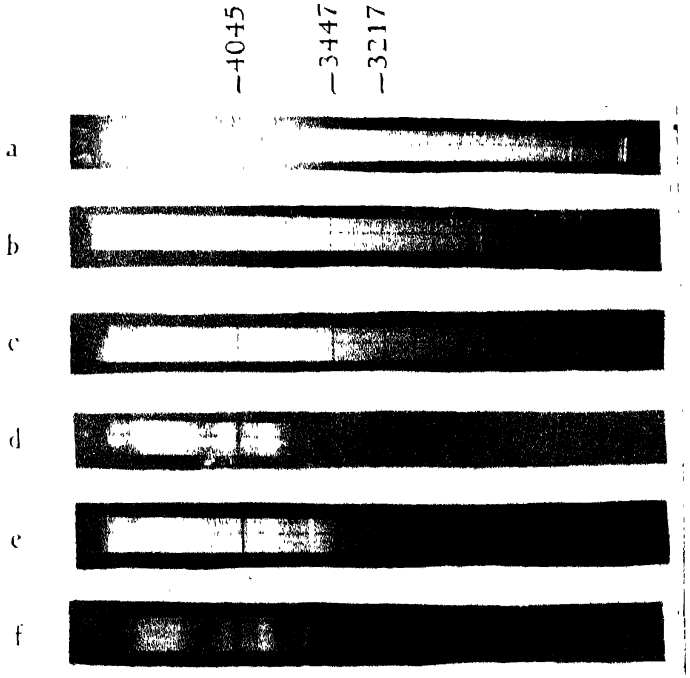
The absorption tube used with potassium vapour was of the usual type with windows cooled by a water jacket.

At first, pressure was varied by varying the temperature, and a number of photographs taken at different pressures. It was found that starting with a very low pressure (below one cm.) the colour of the transmitted light was greenish and the principal series lines showed weak absorption--the higher members could be traced in the spectrogram (*a*) with great difficulty. Gradually increasing the pressure up to 1/2 atmos. the green colour deepened and at the same time the intensity of the absorption lines strengthened (spectrograms *b*, *c*). On further increasing the pressure the colour was very deep (blue in appearance) and the intensity of the transmitted light was also very low, so that a spectrogram (*d*) could be obtained only with long exposure—about half an hour. At this stage beyond a few earlier members there was a continuous absorption similar in appearance to the spectrogram *f*. This general absorption gradually crept towards the long wave-length side as the pressure was further increased. Evidently the general absorption was due to interaction which increased with the increase in the number of interacting centres, the entire mass of vapour approaching to opacity. It was felt that this hypothesis could easily be tested by keeping the partial pressure of potassium low and increasing the total pressure in the chamber by a suitable admixture of some gas which does not present any absorption in the range under consideration. Combination of nitrogen with alkalies being unknown and as nitrogen does not produce any absorption in this region it was thought that nitrogen could be the best gas for such an admixture. Nitrogen prepared by decomposing $NH_4 NO_2$ and passing through fused calcium chloride and caustic soda was therefore used.

With nitrogen the procedure was as follows :—A small quantity of potassium was taken in the tube and it was exhausted. About 1 cm. of nitrogen was then admitted and the tube was heated up till the total pressure reached about 50 cms. The colour would then be deep green. The absorption lines broadened and the limit of continuous absorption shifted towards the longer wave-length side. (Spectrograms *e* and *f*.) On admitting more nitrogen and increasing the temperature the tube would become rather opaque and a very small part of the continuous background came through (Spectrogram *f*).

3. *Results and discussion.*

A number of photographs were taken under varying conditions. Some typical ones are attached in Plate XII. It will be noticed that at very low pressure the continuous absorption on the short wave length side is practically absent and only seven or eight lines are found in absorption. (fig. *a*). Increasing the pressure a little more, the continuous absorption sets in (fig. *b*, *c*.) while the intensity of the absorption lines deepens and their number also increases to fifteen or sixteen—(the original negative shows this distinctly; it is difficult to trace so many in the reproduction). On further increasing the pressure the continuous absorption predominates and the line absorption is masked by the former, so that the number now visible is limited to two. And this happens no matter how the pressure is increased, whether by an admixture of nitrogen or by potassium alone. This makes it definite that the continuous absorption is due to potassium present in an atmosphere of high total pressure. At low



Effect of Pressure on Absorption Spectra.

pressure the effect of neighbouring atoms and molecules is negligible, and the potassium atom absorbs only a discrete amount of energy required for the various interorbital transitions allowed by the quantum process ; a series of discontinuous lines are thus found. At higher pressure the neighbouring system exerts considerable influence by collision or otherwise and the potassium atom can absorb a varying quantity of energy, the excess over that required for an inter-orbital transition being transferred to the neighbouring system ; so that instead of absorption of definite frequencies of radiation, absorption of a short range in the neighbourhood of these definite frequencies takes place ; the cumulative effect of such a process is the development of a continuous absorption stretching over wide limits.

In stellar spectra if the non-appearance of a large number of lines is due to a pressure large enough for preventing the development of higher orbits, the results obtained in the present experiment demand that there will be developed a continuous absorption which will mask the ordinary line absorption. This is however not the case; in some stars more and in some less number of lines are seen without the accompanying continuous absorption.

Besides according to the new mechanics, as the Bohr orbits have no real existence in space, it is difficult to see how the high pressure will prevent the development of lines corresponding to transition to higher orbits. This necessarily suggests that the explanation of the above phenomenon is probably different and somewhat on the following lines.

Suppose we have an enclosure containing a number of atoms. If now we have a continuous radiation falling on it and if for some physical reason the probability of the formation of the nth orbit (either in the Bohr sense or in the sense as conceived by the new mechanics) being developed is much less compared to the probability for the development of the first few orbits, then we shall have very few absorbing centres in which the electron is carried to the *n*th orbit. Hence the *n*th and higher lines will be practically invisible.

From a study of the distribution of intensity of the lines as we go up the series—whether in emission or in absorption—it is found that the earlier members are much more intense and the intensity falls off according to some law of progression. Consequently it is reasonable to conclude that the probability of transfer to the first few orbits is much greater. This view is also borne out theoretically by Einstein and others. Hence with a limited number of absorption centres it is the first few lines that will be developed, and this is what we find at low pressures (Spectrogram *a*). The effect of increase of pressure is to increase the probability of transfer to the orbits corresponding to the higher members. That at comparatively lower pressure less number of lines are observed and to increase the number a somewhat higher pressure is necessary has been observed by one of us long ago.[1]

Hence in view of the present experiment it is just possible that the star α Cygni shows more number of lines, because although it has a low pressure the partial pressure of hydrogen is higher than in Sirius which thereby shows a lesser number of lines.

Description of Figures in Plate XII.

(*a*) Potassium only, pressure 1 cm., colour faint green, exposure 2 mts.
(*b*) Do. pressure 3 ,, ,, pea green ,, 4 ,,
(*c*) Do. ,, 8 ,, ,, deep bluish green ,, 10 ,,
(*d*) Do. ,, 60 ,, ,, deep greenish blue ,, 25 ,,
(*e*) Potassium as in (*b*), nitrogen admitted, total pressure 50 cm. colour almost as in (*d*) but less intense, exposure 20 mts.
(*f*) Potassium as in (*c*), total pressure with nitrogen 1 atmos., almost opaque, exposure 25 mts.

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[1] Proc., Roy Soc., *101*, 539 (1922).

24

The Temperature Variation of the Viscosity of Liquids and its Theoretical Significance.

BY

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(*Received for publication, 20th June, 1930.*)

ABSTRACT.

The formula $\eta = A\, e^{\frac{B}{T}}$ connecting the coefficient of viscosity of a liquid with temperature, proposed on theoretical grounds by Sir C. V. Raman has been examined with reference to the behaviour of over 87 liquids of diverse chemical constitution. The agreement between calculated and observed values is very good, except in the case of a few liquids. The physical significance of the two constants A and B has been discussed, and it is shown that the quantity A is comparable with the viscosity of the substance in the state of vapour. The quantity B has been shown in many cases to be of the same order of magnitude as $\frac{W}{R}$, where W is the molecular latent heat of fusion of the substance. The relationship between the constants and chemical constitution of the substances is pointed out. The variation of the constants in a homologous series is also discussed.

1. *Introduction.*

Some seven years ago, in two notes in "Nature" (April 21st, 1923 and May 5th, 1923) Sir C. V. Raman put forward a theory of viscosity of liquids based on their observed behaviour in respect of light-scattering and X-ray diffraction.

In order to explain the fact that the viscosity of a liquid diminishes rapidly with temperature, while the viscosity of a gas rises with temperature, it was suggested in the first note that the transport of momentum through a liquid takes place in two distinct ways, in part with extreme rapidity by transverse elastic waves as in a solid, and in part by the diffusion movement of the molecules as in a gas, which is a relatively slow process. This involved the assumption that a certain proportion of the molecules in a liquid are in a state approximating to that of a solid and the rest in a mobile or gaseous state. The effective rate of transport of momentum through the liquid depends in the first instance on the proportion between the number of molecules in these two states, and as a first approximation is greater in a liquid than in the vapour in the ratio of $\frac{e^{\frac{E_2}{RT}}}{e^{\frac{E_1}{RT}}}$ where E_2 and E_1 are the energy terms involved in separating molecules of the 'vapour' and 'crystalline' types respectively. Hence the viscosity of the liquid is connected with that of the vapour by the formula

$$\eta_{\text{liquid}} = \eta_{\text{vapour}} \exp. \frac{E_2-E_1}{RT}$$

An equation of the form $\eta = Ae^{\frac{B}{T}}$ has two constants and is found to agree with the observed variation of viscosity with temperature, with remarkable accuracy.

As was pointed out in the two notes, the constants A and B in the above equation are not entirely arbitrary but have a physical significance. The quantity A is comparable with the viscosity of the substance in the state of vapour. From the argument used in deducing the formula, it follows that the quantity B should be of the same order of magnitude as $\frac{W}{R}$, where W is the molecular latent heat of fusion of the substance. The influence of pressure on viscosity was explained in the second note, as due on the one hand to the change in equilibrium between the two types of molecules brought about by pressure, and on the other hand, to the diminution of the free space within the liquid.

Various empirical formulae for the temperature variation of viscosity have been proposed from time to time since Thorpe and Rodgers published their memoirs, but they have little theoretical significance especially in elucidating the mechanism by which momentum is transferred from one point to another in a liquid.

Recently the subject has been receiving a great deal of attention from different workers. Mention may be made of Porter's function

$$f\,(\phi) = \frac{K}{T} + c$$

which becomes identical with Raman's formula if $f(\phi) = \log \phi$, where ϕ is the fluidity of the liquid. Andrade (Nature, March 1st, 1930) and Sheppard (Nature, March 29, 1930 and May 10, 1930) have also independently proposed formulae identical with that of Raman. Attention has been also drawn to a formula proposed by Drucker (Zeit. Phy. Chem. 92, 281, 1918) which may be written as

$$\frac{d \log \phi}{d\,T}$$

He was led to formulate this, taking the analogy from a similar thermodynamic equation, *i.e.*, Van't Hoff isochore. This equation and the results obtained by Drucker are discussed in greater detail in a later portion of this paper.

In view of the theoretical significance of the two-constant formula, and the agreement noticed between observed and calculated values in most cases, it was thought advisable to examine the entire mass of data available from the work of Thorpe and Rodgers and find out the limits of the applicability of the formula. The constants 'A' and 'B' have been evaluated for the various substances in all cases, and interesting relations between the chemical constitution, polarity of the molecules, etc., and these constants are clearly noticeable. The most convenient way of exhibiting the concordance of the facts with the two-constant formula is to plot the relation between $\frac{1}{T}$ and $\log \eta$ on graph paper. The resulting graph is usually a perfect straight line. It has been found that for the 87 liquids examined, deviations occur only in a few cases, and these have been noted. The accompanying table shows the mean values of the constants for substances arranged according to their chemical behaviour.

TABLE I.

VALUES OF CONSTANTS A AND B.

Substance.	$A \times 10^7$	B	Substance.	$A \times 10^7$	B
1. *Hydrocarbons (aliphatic)*			2. *Aromatic hydrocarbons*		
Pentane	899	942	Benzene	954	1235
Isopentane	1380	814	Methyl Benzene	1542	1066
Hexane	798	1067	Ethyl ,,	1793	1059
Isohexane	1458	948	O-xylene	1511	1167
Heptane	787	1145	M-xylene	1552	1042
Isoheptane	1400	964	P-xylene	1557	1089
Octane	705	1257			
Trimethyl-Ethylene	1025	878			
Isoprene	1005	882			
Diallyl	806	1021			

TABLE I—*contd.*

Substance.	A × 10⁷	B
3. *Alcohols*		
Methyl alcohol	743	1282
Ethyl ,,	298	1710
Propyl ,,	110	2209
Isopropyl ,,	31·2	2619
Butyl ,,	10·7	2317
Isobutyl ,,	30·43	2779
Trimethyl carbinol	0·17	4447
Amyl alcohol (active)	26·9	2903
Amyl alcohol (inactive)	57·8	2621
Dimethyl-Ethylcarbinol.	8·88	3166
Allyl alcohol	256	1840
4. *Ethers.*		
Diethyl Ether	1489	808
Me. Propyl ,,	1539	818
Et. Propyl. ,,	1343	925
Dipropyl ,,	1212	1030
Me. Isobutyl ,,	1508	882
Et. Isobutyl ,,	1385	970
5. *Aldehydes & Ketones.*		
Acetaldehyde	1744	745
Dimethyl ketone	1626	876
Me. Et. ketone	1504	977
Di-Ethyl ,,	1640	987
Me-Propyl	1569	1015
6. *Acids.*		
Formic Acid	376	1591
Acetic ,,	688	1224
Propionic ,,	844	1418
Butyric ,,	595	1625
Isobutyric ,,	682	1535
7. *Chlorides*		
Propyl chloride	800	867
Isopropyl	1560	885
Isobutyl ,,	1488	1005
Allyl ,,	816	842
Dichlor methane	2545	838
Ethylenechloride	1540	1172
Ethylidene ,,	1909	951
Chlorofom ,,	2830	877
Carbon Tetrachloride	1326	1262
Dicarbon Tetrachloride	3207	975·

Substance.	A × 10⁷	B
8. *Bromides.*		
Ethyl Bromide	1203	798
Propyl ,,	2318	908
Isopropyl ,,	2026	927
Isobutyl ,,	1848	1037
Allyl. ,,	1797	904
Ethylene dibromide	2193	1275
Propylene ,,	2077	1276
Acetylene ,,	3461	975
Isobutylene dibromide	1514	1449
9. *Iodides.*		
Methyl Iodide	1867	945
Ethyl ,,	1747	1015
Propyl ,,	2620	977
Isopropyl ,,	2296	993
Isobutyl ,,	2062	1101
Allyl Iodide	2533	984
10. *Acid Anhydrides.*		
Acetic anhydride	1598	1180
Propionic ,,	1248	1315
11. *Esters.*		
Methyl Formate	2066	828
Ethyl ,,	743	915
Propyl	1441	1048
Me. acetate	1621	924
Ethyl ,,	1347	1026
Propyl ,,	1214	1133
Ethyl Propionate	1375	1068
Me. Butyrate	1308	1109
Me. Isobutyrate	1360	1064
12. *Sulphur Compounds.*		
Carbon disulphide	4125	640
Me-sulphide	2171	762
Et. ,, ,,	1755	940
Thiophen	1608	1090
13. N_2O_4	1945	899
Bromine	1480	910
Water	206	1832.

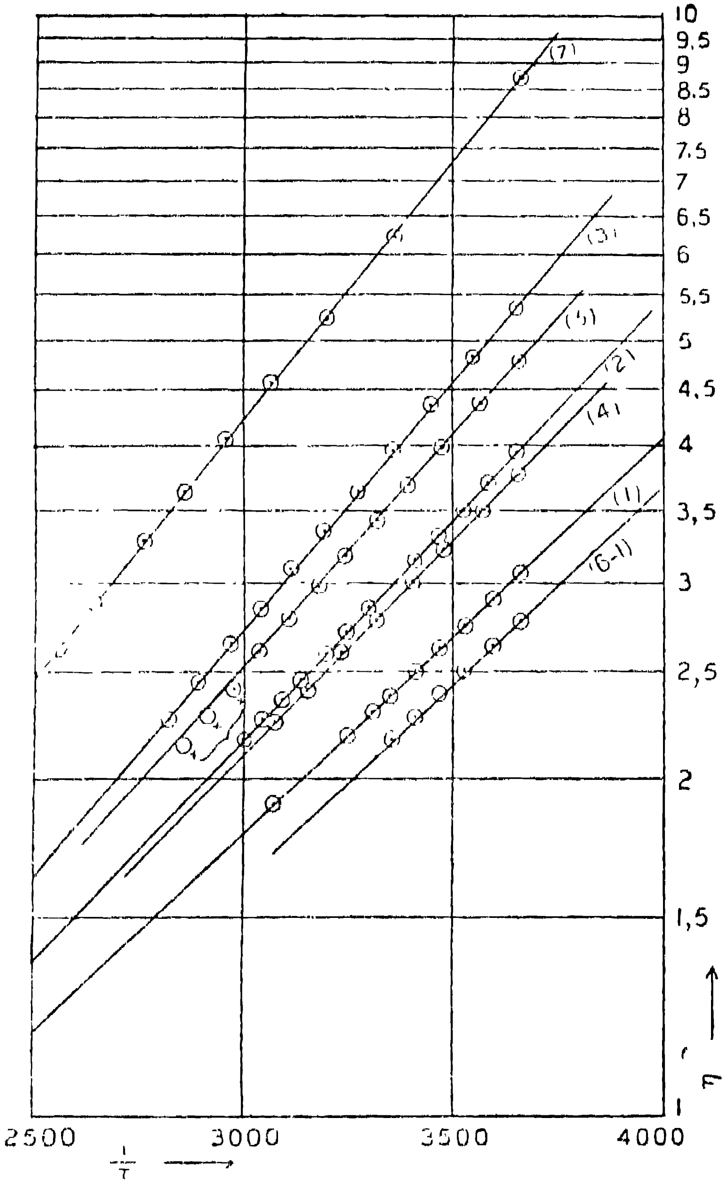

Fig. 1.—Showing relation between viscosity and reciprocal of temperature. Ordinates correspond to logarithmic scale and abscissa to reciprocal of temperature.

1. Me Propyl Ether. 2. Ethyl Propyl Ether. 3. Dipropyl Ether.

4. Me Isobutyl Ether. 5. Ethyl Isobutyl Ether. (6-1) Isopentane

7. Ethyl Benzene.

2. *Dependence of the Constants on Chemical Constitution.*

Aliphatic and Aromatic Hydrocarbons.

On examining the values one notices that as the number of CH_2 groups is increased in a homologous series, the value of B or the slope of log η against $\frac{1}{T}$ curve increases. This can be easily seen from the curves which have been drawn in all cases, and of which the curves in the ether series are reproduced. The iso-compounds have slightly lower values for B than their normal isomers. As between two hydrocarbons containing the same number of carbon atoms, the introduction of a double bond does not very much bring down the value of B. The same effect is noticeable when two double bonds are introduced (*cf.* diallyl and hexane). It may be remarked that a difference of even 30 or 40 units in the value of B does not very much affect the slope of the curve drawn, since B appears in the term $e^{\frac{B}{T}}$. Regarding the value of the constant A, it has the value of the order of 10^{-4} in many cases and a regular gradation in a homologous series can be easily seen. This holds good both for the aliphatic and aromatic series. The values for the iso-compounds are distinctly higher than those of the normal compounds. In general, the value for A increases as a homologous series is ascended. Among the ortho-, meta- and para-xylenes, the differences are not of much significance though the value of B for the ortho compound is higher than those of p- and m-compounds.

Alcohols and Acids.—It is to be noticed that the curves are straight lines excepting in the case of isobutyl alcohol, trimethyl carbinol, amyl alcohol, and dimethyl ethyl carbinol, which show deviations from the straight line relationship. The values for A and B are abnormal in all these cases, particularly in the case of the higher alcohols and acids. This can be connected with the high polarity and association of the molecules. But the formula is still valid in most cases of polar and associated liquids. The accompanying table shows the close concordance between observed and calculated values in the case of two typical fatty acids and the agreement is found to be quite satisfactory.

TABLE II.

Formic acid.			Propionic acid.		
Temp.	Obs.	Cal.	Temp.	Obs.	Cal.
7·59	·02385	·02363	4·70	·01404	·01403
15·96	·01951	·01985	40·04	·00839	·00837
24·16	·01635	·01691	63·63	·00642	·00639
32·86	·01379	·01440	76·70	·00562	·00551
40·36	·01208	·01263	101·01	·00448	·00438
56·30	·00937	·00976	123·67	·00368	·00363
64·20	·00838	·00867	137·05	·00329	·00328
72·05	·00751	·00784			
80·22	·00681	·00692			
89·19	·00619	·00626			
97·23	·00558	·00560			

Alkyl Chlorides, Bromides and Iodides.

The curves show straight line relationship except in the case of isobutyl bromide, isopropyl iodide, ethylene bromide, propylene bromide and isobutylene bromide. On comparing the values of A and B for the halides, interesting relationships become clearly noticeable. The values for both **A** and **B** increase in the order Cl < Br < I. This can be clearly seen from the data for propyl halides given in the tables. As mentioned before, the values of B for the iso-compounds are higher than those for the normal compounds. At the same time, the values of A for the iso-compounds are correspondingly lower. On comparing the values of A and B in the case of CH_2Cl_2, $CHCl_3$ and CCl_4, it is noticed that CCl_4 stands apart from the rest, and this is possibly connected with the non-polarity and symmetrical nature of the molecules of the substance. As in the hydrocarbon series, the introduction of a double bond does not very much affect the value of A and B. This can be seen by comparing the values of propyl and allyl halides.

Ethers.—As we examine a homologous series, we notice an increase in the value of B, and a decrease in the value of A. Isomeric ethers have practically the same value of B.

Aldehydes, Ketones, etc.—Acetaldehyde is characterised by having a low value for B. The data for the homologous series are not available for comparison. The ketones also exhibit the normal gradation in the values. Similarly, the acid anhydrides and esters behave in the normal way.

Sulphur compounds, etc.—In the case of the sulphur compounds, it is noticed that an increase in carbon content results in an increase in B and decrease in A.

Water.—This is a very peculiar substance, and as is well known is highly associated. The curve drawn for water shows considerable deviation from the straight-line relationship, though at higher temperatures the deviations are not very great.

3. *Theoretical Significance of the Constants A and B.*

It is becoming increasingly evident that the viscosity of a liquid depends upon the nature and orientation of molecules. To picture the exact state of affairs, different workers have imagined the existence of different types of molecules. There are two factors which determine the rate of transfer of momentum, on which viscosity depends. (*a*) The equilibrium ratio between the different types of molecular complexes and the simpler molecules. (It is here assumed that there are more than two different types of molecules, depending on the association factor.) (*b*) Their spacial orientation with respect to each other. Both these factors alter with temperature; and hence one is perfectly justified in applying Boltzman's distribution law. The manner in which the equilibrium ratio affects viscosity may be conceived as has been pointed out by Prof. Raman as follows :—When the thickness of the "crystalline" or "rigid" molecules increases, the effective distance through which momentum is transferred is also altered, and hence viscosity increases. If the molecules are associated in a different way, *i.e.*, if they aggregate in the 'end on' position, the increase in viscosity may not be so large as in the previous case. Hence viscosity depends not only on the extent of association of the molecules, but also the manner in which they are associated, and also the way in which the spacial orientation alters with temperature. The abovementioned view of different types of associations existing in a liquid finds support from the recent work of Stewart (Phy. Rev., 35, 726, 1930) who has shown by measurements of X-ray diffraction by octyl alcohols, that when the (OH) group is attached to the end or next to the end of the alcohol molecule, two of these molecules are associated end to end, the length of the chains being in the same straight line, while if the (OH) group is attached to any other carbon atom, the molecules are associated side by side.

If then viscosity (which is a constant for any liquid at a particular temperature) is a factor dependant on the relative proportions of two or more types of aggregate and the manner of their distribution, then the constant can be related to the heat quantities involved in the change.

Oriented and ⟶ Non-oriented and
Large aggregates ⟵ Simpler molecules.

Van't Hoff equation applied to this, leads directly to the formula

$$\frac{d \log \eta}{dT} = \frac{W}{RT^2}$$

Here 'W' represents not only the latent heat of fusion but also the heat quantities involved in the alterations of spacial orientation. The above equation on integration leads to the formula $\eta = Ae^{\frac{W}{RT}}$, and putting $B = \frac{W}{R}$ we get the original equation. Thus we arrive at a definite physical significance for the value of B. In the following tables the values of $\frac{B \times R}{M}$ have been compared with known latent heats of fusion of the substances.

TABLE III.

Relation between $\frac{B \times R}{M}$ *and Latent Heat of Fusion.*

M = mol. wt. of substance in grams. R = 1·985.

Substance.	Latent heat of fusion.	$\frac{B. R}{M}$	Substance.	Latent heat of fusion.	$\frac{B. R}{M}$
Ethylene Bromide	13·0	13·4	Carbon tetra-chloride.	41·1	15·5
Benzene ...	30·2	30·6	Bromoform	10·9	9·4
Acetic acid ...	46·3	43·5	Formic Acid ...	57·4	68·5
Butyric acid ...	28·4	32·1	N_2O_4 ...	34	36
Nitrobenzene ...	22·6	24·8	p-Xylene ...	39·3	20·5
Chloroform ...	19·1	14·6	Water ...	79·5	180
			Methyl alcohol ...	16·2	79·4
Ether ...	27·0	23·0	Ethyl alcohol ...	24·9	73·6
Carbon disulphide	18·8	16·4	Acetone ...	23·1	82·1
Bromine ...	16·2	22·1	Iso propyl alcohol	21·3	86·3
			n-Butyl ,, ...	30·0	62
			Amyl ,, ...	12·4	65·3
			n-Propyl ,, ...	20·6	36·8

From Drucker's paper (*loc. cit.*).

As will be seen from the above table, the value of B represents in some cases nearly the latent heat of fusion of the substance. It is to be observed that large deviations are to be noticed both in associated and non-associated liquids, while in some typical associated liquids the agreement is very good. The agreement is particularly good in the case of the acids while in the case of the alcohols, one notices large deviations. The usual distinction between associated and non-associated liquids fails to hold good in these cases. As has been remarked by Drucker in his paper (*loc. cit.*) the heat absorbed in a change of state represents not only the energy necessary for the disintegration of complex into simpler molecules but also in bringing about a change in the spacial orientation of the molecules. The energy expended for the latter factor is not very considerable.

Physical significance of A.—The constant A corresponds to the mean viscosity of the vapour within the temperature range for which the constant has been evaluated. In the accompanying table the values of A (for a mean temp. of 50° in most cases) have been tabulated along with the known values for the viscosity of the vapour.

TABLE IV.

Comparison of the Values of η (vapour) and A.

Substance.	$\eta \times 10^7$	$A \times 10^7$	Substance.	$\eta \times 10^7$	$A \times 10^7$
Bromine	1510-2480	4480	Ethyl Propionate	880·1161	1375
Benzene	730-1230	954	Me-Isobutyrate	754·1122	1360
Isopentane	870-1150	1380	Prop.-acetate	743·1096	1214
Diethyl Ether	670-1220	1480	Ethyl alcohol	1080·1440	298
Ethyl. Prop. Ether	863	1343	N. Prop. Alcohol	930	119
Di-Prop. Ether	788	1242	Iso. Prop. ,,	1090	81·2
Me-Prop. Ether	946	1539	Prop. Bromide	1190	2310
Ethyl Formate	920	743	Iso.-Prop. ,,	1220	2020
Me-acetate	980-1340	1620	Chloroform	930·1040	2830
Prop.-formate	920	1440	Water vapour	1270·1900	206
			Carbon-disulphide	911·964	4125

It will be noticed that though there is perfect equality between the two quantities only in a few cases, still in the case of most normal liquids the magnitude of the values is of the same order, the value of Λ being generally greater than η and the ratio works out in most cases between 1 and 2. This clearly shows that there is some fundamental relation between the two quantities. In the case of alcohols and water as is to be expected, large deviations are noticeable and the two values are quite incomparable. In the case of carbon disulphide also a large deviation is noticed.

In conclusion it may be pointed out that a correct understanding of the mechanism of transfer of momentum in liquids enables one to have an idea of the nature and orientation of molecules in a liquid.

I wish to thank Sir C. V. Raman, Kt., F.R.S., for his guidance and helpful suggestions throughout the course of this work.

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The Second Spark Spectrum of Krypton

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The spectrum of krypton was first investigated by E. C. C. Baly[1] in 1904. In recent years, L. and E. Bloch[2] and Dejardin have published a number of lines of krypton, after having classified them in three groups marked as 1, 2, and 3, according to the different stages of excitation at which they had appeared. This list comprises not only the lines given by Baly, but also many new lines observed by Bloch and Dejardin who have extended the observational data to λ 2200 A° on the short wave-length side. Lines marked as " 1 " have been classified by P. K. Kichlu[3] and have been proved to be due to singly ionised krypton. The classification of the lines marked as " 2" has been attempted in the following pages, and the analysis, so far as it has been successful, leaves no doubt that these lines are due to doubly ionised krypton. A preliminary note in this connection was published by the present writer, in " Nature " of February 16, 1929.

Experimental

The data with regard to the lines of krypton have been extended by the present writer, to the extreme ultra-violet as far as the furthest limit of transmission of quartz, *viz.*, λ 1900 A°. The source of light used was a quartz tube filled with krypton, obtained from Messrs. E. Leybolds Nachfolger of Germany, and so far as has been ascertained, the tube contains the gas of exceptional purity. This was placed end-on in line with the slit of the spectroscope, and was excited by an induction coil working with a 12 volt supply. The usual method of a spark gap in series and a condenser in parallel with the secondary circuit, was used to give the discharge a condensed character. Up to λ 2100 A°, Hilger's E_2 quartz spectrograph was used ; below this, lines up to λ 1900 A° were photographed with a small Hilger's E_6 quartz spectrograph. Schumann plates were throughout used. Copper arc lines were employed as standard lines up to λ 2100. Below this, silver spark lines were taken as standard. The lines were measured by an Adam Hilger's micrometer, kindly lent to the laboratory, by Principal D. N. Sen ; and wave-lengths were calculated by using Hartmann's three constant dispersion formula. It is believed that the errors in final measurements do not exceed λ·04 A°.

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[1] Phil. Trans., 202, 183, 1904.

[2] Ann. de Phys., 2, 461, 1924.

[3] Proc. Roy. Soc., 120, 643, 1928.

Location of Kr^{++} Spectrum.

The arrangement of electrons in an atom of Kr^{++} may be graphically represented, following Prof. M. N. Saha, in the manner shown below :—

K_1						
2						
	L_1	L_2				
	2	6				
		M_1	M_2	M_3		
		2	6	10		
			N_1	N_2	N_3	N_4
			2	4		
				O_1	O_2	O_3
					P_1	P_2

The most stable structure of a doubly ionised krypton atom, is that when all the four valence electrons are in N_2 level. Other less stable configurations are obtained by putting 3 electrons in N_2 and the fourth one in any of the virtual orbits O_1, O_2, O_3, N_3, etc.

The terms that these different electronic configurations give rise to, may then be calculated on the principles enunciated by Pauli, Heisenberg and Hund. They are given in Table I. We shall here use the notation first proposed by A. Fowler.[1]

TABLE I

Electrons outside rare gas shell.	Configurations.	Prefix Adopted.	Terms.
$4s^2 . 4p^4$	$4N_2$	4p	^3P ^1D ^1S
$4s^2 . 4p^3 . 5s$ $4s^2 . 4p^3 . 6s$	$3N_2O_1$ $3N_2P_1$	5s 6s	^5S ^3S ^3P ^1P ^3D ^1D
$4s^2 . 4p^3 . 5p$	$3N_2O_2$	5p	^5P ^3P ^3P ^3D ^3F ^1P ^1D ^1F ^3S ^3P ^3D ^1S ^1P ^1D
$4s^2 . 4p^3 . 5d$ $4s^2 . 4p^3 . 4d$	$3N_2O_3$ $3N_2N_3$	5d 4d	^5D ^3S ^3P ^3D ^3F ^3G ^1S ^1P ^1D ^1F ^1G ^3P ^3D ^3F ^1P ^1D ^1F

To locate the lines which originate from the terms given above, we have to be guided by

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[1] Proc. Roy. Soc., 117, 317, 1928.

(1) The extension of irregular doublet law to optics, by Saha and Kichlu.[1]

(2) The method of horizontal comparison of spectra, by Saha and Majumdar.[2]

In applying the irregular doublet law, we have to compare the spectra of Se, Br^+, and Kr^{++} all of which will have similar structures. In addition to these, we may also compare the more well-known analogous spectra of Ne^{++} and A^{++}, and then from analogy deduce the position of the spectrum of Kr^{++}. The figures for these are provided in Table II.

TABLE II.

	O	F^+	Ne^{++}
$3L_2\ (M_1 \leftarrow M_2)$ $^5S - {}^5P$	12863 Fowler's Report, P. 168.	25967 Jog, Ind. J. Phys., 2, 344, 1928.	38545 Jog, Ind. J. Phys., 2, 344. 1928.
$3L_2\ (M_2 \leftarrow M_3)$ $^5P - {}^5D$	10788 Fowler's Report, P. 167.	28515 Jog, Unpublished.	40257 Majumdar, Unpublished
	S	Cl^+	A^{++}
$3M_2\ (N_1 \leftarrow N_2)$ $^5S - {}^5P$	10851 Fowler's Report, P. 170.	20854 Paschen, Ann. d. Phys., 71, 560, 1923.	[31200]
$3M_2\ (N_2 \leftarrow N_3)$ $^5P - {}^5D$	11517 Bungartz, Ann. d. Phys., 76, 723, 1925.	25957 Paschen, Ann. d. Phys., 71, 560, 1923.	[40000]

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[1] Saha and Kichlu, Ind. J. Phys., 2, 320, 1928

[2] Saha and Majumdar, Ind. J. Phys., 3, 67, 1928.

	Se	Br^+	Kr^{++}
$3N_2(O_1 \longleftarrow O_2)$ $^5S-{}^5P$	11431 Fowler's Report, P. 171.	21182 S. C. Deb, Proc. Roy. Soc., 127, 197, 1930	[31000]
$3N_2(O_2 \longleftarrow O_3)$ $^5P-{}^5D$	[10000]	21179 S. C. Deb, Proc. Roy. Soc., 127, 197, 1930.	[40000]

From this table, we find that 5s ^5S—5p ^5P lines due to the transition $3N_2(O_1 \longleftarrow O_2)$ will lie at about 31000. Further, it may also be remarked that ^5D separations for O, F^+ and Ne^{++} have not yet deen determined, being too small to be easily resolvable. Paschen[1] finds that in Cl^+ they are of the order of one frequency unit. In Br^+, Mr. S. C. Deb[2] finds that they are of the order of 30. In Kr^{++}, we should therefore expect that they will be fairly large, especially because the stage of ionisation is increased one step further than in Br^+. In a similar way, the ^5P separations of Br^+, as found by Mr. S. C. Deb, are of the order of 100. The corresponding separations of Kr^{++} may therefore, be expected to be at least of the order of 200.

Further clue to the disentanglement of this spectrum, as has been said before, is supplied by the method of horizontal comparison of Saha and Majumdar, which states that the lines originating from the same transitions of electrons in successive atoms, as given in the periodic table, are in arithmetic progression, provided, however, that the transitions take place between orbits with the same total quantum number.

We compare the spectra of

O^{++}	F^{++}	Ne^{++}
S^{++}	Cl^{++}	A^{++}
Se^{++}	Br^{++}	Kr^{++}

The data are given in Table III.

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[1] Ann. d. Phys., 71, 792, 1923.

[2] Proc. Roy. Soc., 127, 197, 1930,

TABLE III.

	O^{++}	F^{++}	Ne^{++}
XL_2 $(M_1 \longleftarrow M_2)$	29925 Fowler, Proc. Roy. Soc., 187, 325, 1928.	34410 Dingle, Proc. Roy. Soc., 122, 144, 1929.	38545 Jog, Ind. J. Phys., 2, 344, 1928.
XL_2 $(M_2 \longleftarrow M_3)$	31911 Fowler, Proc. Roy. Soc., 117, 325, 1928.	38748 Dingle, Proc. Roy. Soc., 122, 144, 1929.	46257 Majumdar, Unpublished.
	S^{++}	Cl^{++}	A^{++}
XM_2 $(N_1 \longleftarrow N_2)$	26047 J. Gilles, Comp. Ren., 188, 63, 1929.	30030 Bowen, Phys. Rev., 31, 35, 1928.	[31200]
XM_2 $(N_2 \longleftarrow N_3)$	36263 J. Gilles, Comp. Ren., 21st Jan., 1929, P. 321.	37501 Bowen, Phys. Rev., 31, 34. 1928	[39000]
	Se^{++}	Br^{++}	Kr^{++}
XN_2 $(O_1 \longleftarrow O_2)$	23979 D. K. Bhattacharya, Nature, August 10, 1929.	28063 S. C. Deb, Proc. Roy. Soc., 127, 197, 1930.	[31000]
XN_2 $(O_2 \longleftarrow O_3)$	[34000]	37340 S. C. Deb, Proc. Roy. Soc., 127, 197, 1930.	[40000]

Thus from the two tables, we can at once predict that the positions of $5s\ {}^5S—5p\ {}^5P$ and $5p\ {}^5P—5d\ {}^5D$ lines would lie at about 31000 and 40000 frequency units respectively. These lines will be the strongest in the regions where they occur, especially the $5s\ {}^5S—5p\ {}^5P$ lines.

Further, let us compare the spectra of As^{++} and Y^{++}. The term values of O_1, P_1, and O_2 of Y^{++} are given by Millikan and Bowen,[1] The values of the corresponding terms in As^{++} can be calculated from the classification given by Lang.[2]

Thus we have

	As^{++} ($v=0$)	Y^{++} ($x=6$)
xN_2O_1	120000	157822
xN_2P_1	66000	78572
xN_2O_2	95000	122335

For Kr^{++} ($x=3$), we should therefore, expect that the corresponding terms will lie at the arithmetic means of the above two sets,

Thus

	Kr^{++} ($x=3$)
$3\ N_2O_1$	140000
$3\ N_2P_1$	72000
$3\ N_2O_2$	110000

Hence the transition $3\ N_2\ (O_1 \longleftarrow O_2)$ will give rise to lines at 30000, and lines due to $3N_2\ (O_2 \longleftarrow P_1)$ will lie at 38000.

To locate the lines due to the transition $3N_2\ (N_3 \longleftarrow O_2)$ is rather difficult; because no law has yet been found to be applicable to this transition. Mr. S. C. Deb finds that in Br^+ these lines are more towards the ultra-violet than the lines due to $3N_2\ (O_1 \longleftarrow O_2)$. We should therefore search for these lines in the region 27000.

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[1] Phys. Rev., 28, 923, 1926.

[2] Phys. Rev., 32, 737, 1928.

The most intense line at 31000 is 30801·3 (10). This was therefore taken to be the 5s $^5S_2$—5p $^5P_3$ line. The two other strong lines in this region with suitable separations, are 30557·0 (4) and 30424·6 (4). Assuming these to represent the 5s $^5S_2$—$^5p_2$ line, the two other strong lines region, with suitable separations are 30557·0 (4) and 30424·6 (4). Assuming these to represent the 5s $^5S_2$—5p $^5P_2$ and 5s $^5S_2$—5p $^5P_1$ lines, the other multiplets emerged without much difficulty, in the predicted regions.

The Multiplets.

$3N_2O_2 \longrightarrow$	$5p^5P_1$	132·6	$5p^5P_2$	243·8	$5p^5P_3$
$3N_2O_1 \longrightarrow 5s\ ^5S_2$	30424·6 (4)		30557·0 (4)		30801·3 (10)
$3N_2O_3 \longrightarrow 5d\ ^5D_0$	39801·1 (1)		...		...
215·1					
$5d\ ^5D_1$	40016·2 (2)		39883·1 (3)		...
141·6					
$5d\ ^5D_2$	40158·0 (3)		40024·5 (3)		39782·1 (2)
226·5					
$5d\ ^5D_3$	...		40251·7 (3)		40008·0 (1)
200·1					
$5d\ ^5D_4$	...		...		40208·1 (3)
$3N_2P_1 \longrightarrow 6s\ ^5S_2$	37440·8 (1)		37307·5 (3)		37063·0 (5)
$3N_2N_3 \longrightarrow 4d\ ^5D_0$	27162·6 (1)				
118·7					
$4d\ ^5D_1$	27013·9 (1)		27176·4 (2)		...
215·6					
$4d\ ^5D_2$	26828·7 (0)		26960·5 (1)		27204·6 (2)
116·8					
$4d\ ^5D_3$	...		26843·7 (2)		27087·4 (4)
203·9					
$4d\ ^5D_4$	...		...		26888·9 (8)

Ionisation Potential of Kr^{++}

From the above multiplets, we have,

taking the line $5s\,^5S_2 - 5p\,^5P_3$, $O_1 - O_2 = 30801$,

and taking the line $5p\,^5P_3 - 6s\,^5S_2$, $O_2 - P_1 = 37063$,

therefore $\longrightarrow O_1 - P_1 = 67864$.

Thus, assuming $O_1 = 9N/(2+\sigma)^2$ and $P_1 = 9N/(3+\sigma)^2$, we have, from the table of Rydberg sequences, given in Fowler's report,

$O_1 = 142812$ and $P_1 = 64948$.

Hence $O_2 = 112011$.

If we take $O_2 = 9N/(2+\pi)^2 = 112011$,

we must have $N_2 = 9N/(1+\pi)^2 = 254718$.

Corresponding to this value of N_2, we have the ionisation potential equal to 31·4 volts.

It seems to be a general rule, as illustrated by the data in the following table taken from Saha and Kichlu's paper, [1] that, as the degree of ionisation is increased, the lines due to transitions between two higher electronic configurations, continuously shift towards the higher frequency side with respect to the lines due to transitions between two preceding electronic levels.

	$M_1 \longleftarrow M_2$ $^2S_1 - {}^2P_1$	$M_2 \longleftarrow M_3$ $^2P_2 - {}^2D_2$
Na	16956	12199
Mg^+	35669	35730
Al^{+2}	53680	62037
Si^{+3}	71280	88672
P^{+4}	88619	114755
S^{+5}	105866	140313

This rule is borne out by the quintet-quintet mutiplets of this classification and holds also for the analysis attempted later on.

A reference to the table of theoretical terms given before, will show that in addition to the quintet terms, we expect also a large number of triplet and singlet terms. The attempt to discover them, has only been partially successful, inasmuch as though the evidence for the existence of a large number of terms has been obtained, it has not been found possible to effect their identification. Table IV contains a list of all these terms, whose values merely represent differences with respect to the deepest level a_1 of this set. The nomenclature is purely arbitrary.

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[1] Ind. J. Phys., 2, 324, 1928.

TABLE IV.

Term values.	Nomenclature.	Term values.	Nomenclature.
0	α_1	40475 3	β_{14}
717.3	α_2	42666.7	β_{15}
2911.6	α_3	42742.5	β_{16}
3346.6	α_4	43351.1	β_{17}
3861.8	α_5	43554.6	β_{18}
4969.2	α_6	44123.9	β_{19}
4999.6	α_7	44253.9	β_{20}
6123.0	α_8	45407.9	β_{21}
8101.3	α_9	...	...
28642.8	β_1	76932.1	γ_1
30801.3	β_2	77402.3	γ_2
33361.6	β_3	77561.7	γ_3
33771.3	β_4	77665.6	γ_4
34825.6	β_5	77803.2	γ_5
35188.6	β_6	78561 6	γ_6
35555 1	β_7	78666.6	γ_7
35858.4	β_8	78972.2	γ_8
35982.5	β_9	79971.2	γ_9
38409.2	β_{10}	81865.2	γ_{10}
39797.3	β_{11}	82126.2	γ_{11}
40385.7	β_{12}	...	...
40419.6	β_{13}	...	...

In this list α's combine with β's and β's combine with γ's. For reasons stated before, the strong group of lines about the region 31000, are presumably due to transition $3N_2(O_2 \leftarrow O_2)$, and since the transitions between α's and β's explain a large number of these lines, the former are the terms obtained from the configuration $3N_2O_1$, and the latter from $3N_2O_2$. The probability of some of the α terms coming from $3N_2N_3$, is not excluded. The terms designated as γ_1, γ_2, etc., obviously owe their origin to $3N_2O_3$ or $3N_2P_3$.

Table V contains the complete list of the classified lines, in addition to the new lines measured during the course of the present investigation.

TABLE V.

λ (I.A.)	I	ν (vac.)	Classification	Ob-server	If measured by another observer
4404·30	1	22698·7	$\alpha_9 - \beta_2$	B	
4223·06	1	23672·9	$\alpha_6 - \beta_1$	Bl	
3957·67	3	25260·3	$\alpha_9 - \beta_3$	B	
3952·02	1	25296·5	$\alpha_4 - \beta_1$	B	
3884·16	1	25732·1	$\alpha_3 - \beta_1$	B	
3740·72	2	26725·2	$\alpha_9 - \beta_5$	Bl	
3726·30	0	26828·7	$4d^5D_2 - 5p^5P_1$	B	
3724·21	2	26843·7	$4d^5D_3 - 5p^5P_2$	B	
3718·64	8	26883·9	$4d^5D_4 - 5p^5P_3$	B	
3708·08	1	26960·5	$4d^5D_2 - 5p^5P_2$	B	
3696·65	1	27043·9	$4d^5D_1 - 5p^6P_1$	B	
3690·65	4	27087·8	$4d^6D_3 - 5p^5P_3$	B	
3680·49	1	27162·6	$4d^5D_0 - 5p^5P_1$	Bl	
3678·62	2	27176·4	$4d^5D_1 - 5p^6P_2$	Bl	
3674·81	2	27204·6	$4d^5D_2 - 5p^5P_3$	Bl	
3670·23	1	26238·5	$\alpha_8 - \beta_3$	Bl	
3641·33	4	27454·7	$\alpha_4 - \beta_2$	B	
3615·82	3	27648·4	$\alpha_8 - \beta_4$	B	
3579·96	1	27925·3	$\alpha_2 - \beta_1$	Bl	
3524·78	0	28363·5	$\alpha_7 - \beta_3$	B	
3521·12	1	28391·9	$\alpha_6 - \beta_3$	B	
3474·64	6	28771·7	$\alpha_7 - \beta_4$	B	
3471·01	1	28801·8	$\alpha_6 - \beta_4$	Bl	
3439·46	6	29066·0	$\alpha_8 - \beta_6$	B	
3396·58	3	29433·0	$\alpha_8 - \beta_7$	B	
3388·92	3	29499·5	$\alpha_5 - \beta_3$	Bl	

λ (I.A.)	I	ν (vac.)	Classification	Ob-server	If measured by another observer
3351·93	8	29825·0	$\alpha_7-\beta_5$	B	
3348·14	1	29858·8	$\alpha_6-\beta_5$	B	
3342·45	6	29909·6	$\alpha_5-\beta_4$	B	
3330·74	6	30014·8	$\alpha_4-\beta_3$	B	
3311·45	5	30189·5	$\alpha_7-\beta_6$	B	
3308·14	3	30219·8	$\alpha_6-\beta_6$	B	
3285·87	4	30424·6	$5s^5S_2-5p^5P_1$	B	
3271·63	4	30557·0	$5s^5S_2-5p^5P_2$	B	
3268·47	6	30586·6	$\alpha_6-\beta_7$	B	
3245·69	10	30801·3	$5s^5S_2-5p^5P_3$	B	
3239·51	7	30860·0	$\alpha_7-\beta_8$	B	
3223·53	1	31013·0	$\alpha_6-\beta_9$	B	
3191·20	5	31327·1	$\alpha_5-\beta_6$	B	
3175·65	1	31480·5	$\alpha_4-\beta_5$	B	
3170·93	3	31527·3	$\beta_{21}-\gamma_1$	B	
3139·58	2	31842·1	$\alpha_4-\beta_6$	B	
3124·40	5	31996·9	$\alpha_5-\beta_8$	B	
3112·24	5	32120·9	$\alpha_5-\beta_9$	B	
3103·88	0	32208·4	$\alpha_4-\beta_7$	B	
3097·15	5	32278·3	$\alpha_3-\beta_6$	B	
3096·47	1	32285·4	$\alpha_9-\beta_{12}$	B	
3063·14	5	32636·7	$\alpha_4-\beta_9$	B	
3062·43	1	32644·3	$\alpha_3-\beta_7$	B	
3046·93	5	32810·3	$\beta_{19}-\gamma_1$	B	
3024·45	6	33054·3	$\alpha_2-\beta_4$	B	
2996·64	2	33361·0	$\alpha_1-\beta_3$	B	
2992·24	5	33410·0	$\alpha_7-\beta_{10}$	B	
2979·83	1	33549·1	$\beta_{20}-\gamma_5$	B	
2968·32	3	33679·2	$\beta_{19}-\gamma_5$	B	

λ (I.A.)	I	ν (vac.)	Classification	Ob-server	If measured by another observer
2960·15	0	33772·2	$\alpha_1-\beta_4$	B	
2930·92	2	34109·0	$\alpha_2-\beta_5$	B	
2930·61	2	34112·6	$\beta_{18}-\gamma_4$	R	
2917·70	2	34263·6	$\alpha_8-\beta_{12}$	B	
2913·24	0	34316·0	$\beta_{17}-\gamma_4$	B	
2900·08	4	34471·7	$\alpha_2-\beta_6$	B	
2893·70	5	34547·7	$\alpha_5-\beta_{10}$	B	
2892·19	8	34565·7	$\alpha_9-\beta_{15}$	B	
2872·88	1	34798·0	$\alpha_7-\beta_{11}$	B	
2870·62	6	34825·4	$\alpha_1-\beta_5$	B	
2856·09	1	35002·3	$\beta_{15}-\gamma_4$	B	
2851·18	5	35062·9	$\alpha_4-\beta_{10}$	B	
2840·99	5	35188·6	$\alpha_1-\beta_6$	B	
2835·97	1	35250·8	$\alpha_9-\beta_{17}$	B	
2822·64	1	35417·3	$\alpha_6-\beta_{12}$	B	
2819·89	0	35451·3	$\alpha_6-\beta_{13}$	B	
2811·80	3	35555·1	$\alpha_1-\beta_7$	B	
2784·9	0	35897·	$\beta_{15}-\gamma_6$	B	
2781·9	0	35936·	$\alpha_5-\beta_{11}$	B	
2778·24	1	35983·4	$\alpha_1-\beta_9$	B	
2742·57	3	36451·4	$\alpha_4-\beta_{11}$	B	
2742·03	0	36458·6	$\beta_{21}-\gamma_{10}$	B	
2736·9	0	36527·	$\alpha_5-\beta_{12}$	B	
2730·45	1	36613·2	$\alpha_5-\beta_{14}$	B	
2729·92	1	36620·2	$\alpha_8-\beta_{16}$	Bl	
2710·27	1	36885·8	$\alpha_3-\beta_{11}$	Bl	
2700·63	1	37017·5	$\beta_{12}-\gamma_2$	Bl	
2697·31	5	37063·0	$5p^5P_3-6s^6S_2$	B	
2696·61	5	37072·6	$\alpha_4-\beta_{13}$	B	
2692·55	2	37128·5	$\alpha_4-\beta_{14}$	B	

λ (I.A.)	I	ν (vac.)	Classification	Observer	If measured by another observer
2691·84	1	37137·3	$\beta_{11}-\gamma_1$	B	
2679·63	3	37307·5	$5p^5P_2-6s^5S_2$	B	
2670·68	5	37432·5	$\alpha_8-\beta_{18}$	B	
2670·09	1	37440·8	$5p^5P_1-6s^5S_2$	B	
2661·24	1	37565·3	$\alpha_3-\beta_{14}$	Bl	
2653·97	1	37668·2	$\alpha_7-\beta_{15}$	B	
2648·70	4	37743·1	$\alpha_7-\beta_{16}$	B	
2639·76	6	37870·9	$\beta_{20}-\gamma_{11}$	B	
2630·66	4	38001·8	$\alpha_8-\beta_{19}$	B	
2624·82	2	38086·6	$\beta_{14}-\gamma_6$	B	
2609·41	0	38311·4	$\beta_{18}-\gamma_{10}$	B	
2606·61	0	38352·5	$\alpha_7-\beta_{17}$	B	
2604·63	3	38381·7	$\alpha_6-\beta_{17}$	B	
2596·74	1	38498·4	$\beta_{14}-\gamma_8$	B	
2590·74	1	38587·5	$\alpha_6-\beta_{18}$	Bl	
2578·9	0	38764·	$\beta_{11}-\gamma_6$	B	
2571·21	3	38880·6	$\alpha_5-\beta_{16}$	B	
2557·99	2	39081·5	$\alpha_2-\beta_{11}$	B	
2555·14	4	39125·1	$\alpha_7-\beta_{19}$	B	
2553·17	3	39155·3	$\alpha_6-\beta_{19}$	B	
2544·70	1	39285·6	$\alpha_8-\beta_{21}$	B	
2538·34	1	39284·1	$\beta_{16}-\gamma_{11}$	B	
2537·58	3	39395·7	$\alpha_4-\beta_{16}$	B	
2517·93	2	39703·2	$\alpha_2-\beta_{13}$	B	
2512·94	2	39782·1	$5p^5P_3-5d^5D_2$	B	
2511·74	1	39801·1	$5p^5P_1-5d^5D_0$	B	
2506·57	3	39883·1	$5p^5P_2-5d^5D_1$	B	
2498·75	1	40008·0	$5p^5P_3-5d^5D_3$	B	

λ (I.A.)	I	ν (vac.)	Classification	Observer	If measured by another observer
2498·23	2	40016·2	$5p^5P_1-5d^5D_1$	B	
2497·72	3	40024·5	$5p^5P_2-5d^5D_2$	B	
2489·42	3	40158·0	$5p^5P_1-5d^5D_2$	B	
2486·31	3	40208·1	$5p^5P_3-5d^5D_4$	B	
2483·62	3	40251·7	$5p^5P_2-5d^5D_3$	B	
2483·23	3	40258·0	$\beta_{10}-\gamma_7$	B	
2483·00	1	40261·7	$\alpha_5-\beta_{19}$	Bl	
2478·81	2	40329·8		A	
2477·76	0	40346·8		A	
2474·91	3	40393·5	$\alpha_5-\beta_{20}$	B	
2474·79	2	40395·2		A	2474·71 (B)
2473·98	2	40408·7	$\alpha_7-\beta_{21}$	B	
2473·53	0	40415·8		A	
2473·31	1	40419·6	$\alpha_1-\beta_{13}$	B	
2472·18	0	40437·9	$\alpha_6-\beta_{21}$	A	2472·16 (B)
2470·59	0	40463·9		A	2470·42 (B)
2468·60	1	40496·5		A	2468·48 (B)
2467·05	0	40522·0		A	2466·92 (B)
2464·72	9	40560·3		A	
2463·35	0	40582·8		A	
2462·57	0	40595·7		A	
2459·66	2	40643·9	$\alpha_3-\beta_{18}$	B	
2456·01	8	40704·1		A	
2455·20	0	40717·5		A	
2454·32	0	40732·1		A	
2453·32	0	40748·8		A	
2452·30	3	40765·7		A	2452·30 (B)

λ(I.A.)	I	ν (vac.)	Classification	Obser-ver	If measured by another observer
2451·62	2	40777·0	$\alpha_4-\beta_{19}$	B	
2446·36	5	40864·6		A	
2439·70	3	40976·2		A	2439·56 (Bl)
2436·49	1	41030·2		A	
2429·84	1	41142·5		A	2429·72 (B)
2428·28	8	41168·9		A	
2426·24	7	41203·5		A	
2425·08	1	41223·2		A	2425·07 (B)
2422·50	0	41267·1		A	2422·42 (B)
2420·20	2	41306·3		A	
2418·29	3	41338·9		A	
2418·05	3	41343·1	$\alpha_3-\beta_{20}$	B	
2414·86	5	41397·7		A	
2413·63	3	41418·8	$\beta_9-\gamma_2$	A	
2409·04	4	41497·7		A	
2408·43	1	41508·4		A	
2406·34	2	41544·3	$\alpha_5-\beta_{21}$	B	
2400·22	1	41650·1	$\beta_{14}-\gamma_{11}$	B	
2399·09	1	41669·7		A	
2398·37	1	41682·3		A	2398·30 (B)
2397·01	2	41705·9	$\beta_{13}-\gamma_{11}$	B	
2394·82	0	41744·1	$\beta_6-\gamma_1$	B	
2392·79	4	41779·4		A	
2390·49	3	41819.6	$\beta_9-\gamma_5$	A	
2382·12	6	41966·6*		A	
2376·77	0	42061·1	$\alpha_4-\beta_{21}$	B	
2373·69	2	42115·6		A	
2368·89	2	42201·0		A	
2368·22	1	42212·9	$\beta_6-\gamma_2$	B	

λ (I.A.)	I	ν(vac.)	Classification	Observer	If measured by another observer
2365·60	2	42259·0		A	
2362·69	4	42311·7		A	
2353·60	10	42475·1		A	
2352·66	1	42492·0		A	
2348·06	0	42575·3		A	
2344·29	8	42643·8		A	
2343·03	1	42666·7	$\alpha_1-\beta_{15}$	B	
2340·85	1	42706·4	$\beta_8-\gamma_6$	B	
2339·07	0	42738·9	$\beta_5-\gamma_3$	B	
2320·88	1	43073·9		A	2320·84 (B)
2316·25	6	43159·9	$\beta_4-\gamma_1$	A	2316·21 (B)
2315·46	6	43174·7		A	2315·37 (B)
2311·96	6	43240·0		A	2311·89 (B)
2301·76	3	43457·9	$\beta_{10}-\gamma_{10}$	A	2301·61 (B)
2291·19	2	43632·0	$\beta_4-\gamma_2$	B	
2287·76	7	43697·3		A	2287·68 (B)
2283·00	7	43788·5		A	
2282·85	3	43791·3	$\beta_1-\gamma_3$	A	2282·85 (B)
2276·67	1	43910·2		A	
2273·22	4	43976·8		A	2273·08 (B)
2263·81	0	44159·6		A	
2250·21	2	44426·5		A	2250·15 (B)
2245·44	2	44520·9		A	
2236·68	0	44695·2		A	
2234·61	0	44736·6		A	
2232·19	0	44784·9	$\beta_6-\gamma_9$	B	
2227·98	4	44869·7		A	2227·89 (B)
2225·19	1	44925·9		A	
2221·88	0	44992·9		A	
2215·78	0	45116·7		A	

λ (I.A.)	I	γ (vac.)	Classification	Observer	If measured by another observer
2211·86	1	45196·7		A	
2211·68	3	45200·4	$\beta_4-\gamma_8$	A	
2208·42	1	45267·1		A	
2206·57	0	45305·0	$\beta_3-\gamma_7$	A	
2202·61	1	45386·5		A	
2201·30	1	45413·5		A	
2197·46	3	45492·8		A	
2186·79	0	45714·8		A	
2182·10	0	45813·0		A	
2177·94	0	45900·5		A	
2173·68	1	45990·5		A	
2172·04	0	46025·2		A	
2170·69	0	46053·8		A	
2169·14	1	46086·7		A	
2167·69	1	46117·5		A	
2165·95	0	46154·6		A	
2161·00	0	46260·3		A	
2150·72	1	46481·4		A	
2147·56	0	46549·7		A	
2145·00	2	46605·3		A	
2144·75	6	46610·8	$\beta_3-\gamma_9$	A	
2143·38	0	46640·5		A	
2139·34	2	46728·6		A	
2134·00	0	46845·5		A	
2132·84	1	46871·0		A	
2131·15	0	46908·1		A	
2129·81	0	46937·7	$\beta_6-\gamma_{11}$	A	
2129·67	2	46940·7		A	
2128·81	2	46959·7		A	

λ (I.A.)	I	γ (vac.)	Classification	Observer	If measured by another observer
2124·88	0	47046·5		A	
2119·95	0	47155·9		A	
2118·71	4	47183·5		A	
2117·78	9	47204·2		A	
2114·19	0	47284·4		A	
2112·38	0	47324·9		A	
2110·79	0	47360·6		A	
2109·73	2	47384·4		A	
2106·04	0	47467·4		A	
2100·59	0	47590·5		A	
2099·41	1	47617·2		A	
2096·90	8	47674·2		A	
2095·84	1	47698·3		A	
2094·41	6	47730·9		A	
2093·07	0	47761·4	$\beta_2-\gamma_6$	A	
2091·55	0	47796·1		A	
2089·94	10	47833·0		A	
2088·57	5	47864·3	$\beta_2-\gamma_7$	A	
2086·87	1	47903·3		A	
2086·29	0	47916·6		A	
2084·10	2	47967·0		A	
2083·46	1	47981·7		A	
2081·72	6	48021·8		A	
2078·58	0	48094·4	$\beta_4-\gamma_{10}$	A	
2078·19	0	48103·4		A	
2077·57	0	48117·7		A	
2076·46	1	48143·5		A	
2075·63	0	48162·9		A	
2073·88	3	48203·3		A	

λ (I.A.)	I	ν (vac.)	Classification	Obser-ver	If measured by another observer
2071·05	0	48269·2		A	
2068·80	0	48319·6		A	
2066·13	3	48384·1		A	
2065·28	0	48404·0		A	
2064·01	0	48433·8		A	
2063·00	0	48457·5		A	
2062·20	0	48476·3		A	
2062·05	1	48479·8		A	
2060·71	0	48511·4		A	
2059·45	1	48541·0		A	
2058·75	4	48557·8		A	
2057·29	0	48592·0		A	
2056·74	0	48605·0		A	
2054·47	0	48659·7		A	
2053·33	1	48685·7		A	
2052·49	0	48705·6		A	
2050·00	3	48764·8	$\beta_3-\gamma_{11}$	A	
2047·19	1	48831·6		A	
2040·24	2	48998·0		A	
2036·64	0	49084·6		A	
2035·15	0	49120·6		A	
2033·13	2	49169·4	$\beta_2-\gamma_9$	A	
2018·92	3	49515·4		A	
2005·41	0	49848·9		A	
2004·33	2	49875·8		A	
1992·96	0	50160·2		A	
1981·96	0	50438·5		A	
1974·59	3	50626·7		A	
1973·47	1	50655·5		A	
1962·70	2	50933·4		A	

γ (I.A.)	I	ν (vac.)	Classification	Obser-ver	If measured by another observer
1961·84	1	50955·7		A	
1947·75	2	51324·2	$\beta_2-\gamma_{11}$	A	
1932·92	0	51718·0		A	
1931·33	2	51760·6		A	
1930·39	2	51785·8		A	

Explanation of the table:—

In the 1st column, the wave-lengths of all classified lines and also of all new lines measured by the present writer, are given in international Angstrom. The 2nd column gives the intensity of the lines. In the 3rd column, the wave-numbers of the lines are given, after having reduced them to vacuum. The 4th column gives the classification. The name of the observer is given in the 5th column. "B" denotes Bloch, "Bl" Baly, and "A" the present writer. The 6th column shows if any line has been measured by any other observer.

I wish to record my heartiest thanks to Prof. P. K. Kichlu of the Govt. College, Lahore, who has always helped me at all stages of this investigation. I am also extremely grateful to Prof. M. N. Saha, F. R. S., for his helpful criticisms and his kind interest in my work. My best thanks are also due to Principal D. N. Sen for his having kindly encouraged me in my work, and for having lent his micrometer to the laboratory ; but for this, the measurement of krypton lines would not have been possible. I wish also to thank Prof. S. N. Roy for affording me all facilities in the laboratory.

Behar National College,
Patna.

On the Spectrum of Doubly Ionised Thallium.

BY

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(*Received for publication, 18th July, 1930.*)

(Plate XIII.)

ABSTRACT.

The paper gives an account of the experimental work which has led to an extension of our knowledge of the second spark spectrum of thallium. In accordance with the theory of spectra developed by Hund, it has been shown that the spectrum consists of two parts, an ordinary doublet spectrum, and a quartet, doublet spectrum, with the lowest term, the metastable inverted ^2D. The two types of ion on which these two spectra are built are (d^{10}) and (d^9s) which are spectroscopically terms of the type ^1S and ^3D and ^1D. A catalogue of all the lines with their designations is given.

1. *Introduction.*

Continuing the previous work[1] of one of the authors on the structure of the spectra of singly ionised thallium and doubly ionised lead, the spectra of Tl III and Pb IV have been under examination by us for some time past.

The term structure of the second spark spectrum of thallium (Tl III) should be similar in character to that of any chemically analogous atom or ion. Of these, the spectra of Ag I, Cu I, and Au I; Zn II, Cd II, and Hg II and Ga III and In III have already been analysed to some extent. The first attempt to identify any of the lines belonging to Tl III was made by Caroll,[1] who identified the first members of the S P D sequence. By analogy with the spectra of Ga III and In III it was thought that in this case the chief members of the secondary series would be in the visible and quartz regions and as such would readily yield themselves for examination under varying conditions of excitation. The identification and location of these was also greatly fecilitated by our knowledge of the corresponding members in Ga III and In III and those in Au I and Hg II.

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[1] Ind. J. Phy., II, 467, (1928).

Corresponding to the addition of an electron to the three different states of Tl IV core, three distinct families of terms arise as shown in the following table :

TABLE I.

K L M N	O					P			Term	Predicted
1_1……………4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	prefix	terms
60	2	6	10			(1)			6s	^2S
60	2	6	10				(1)		6p	^2P
60	2	6	10					(1)	6d	^2D
60	2	6	9			1 (1)			6s′	^2D
60	2	6	9			1	(1)		6p′	$^4P\ D\ F$ $^2P\ D\ F$ $^2P\ D\ F'$
60	2	6	9			1		(1)	6d′	$^4S\ P\ D\ F\ G$ $^2S\ P\ D\ F\ G$ $^2S\ P\ D\ F\ G'$

Mention was made in a recent paper[2] that a preliminary attempt by the application of the X-ray doublet laws revealed a number of regularities consisting of the regular doublet terms, in thallium III.

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[1] Phil. Trans. (A) 225, 357, (1926).

[2] Zeit. fur. Phys., 61, 149, (1930).

The analysis of Cu I and Au I and that of Hg II has shown that in addition to the ordinary doublet systems built on the ion (d^{10}) there is yet another important family of terms built on (d^9s) which is characterised by doublet and quartet terms. The deepest term of this system is a metastable ^2D term (d^9s^2) and it should be inverted and very low.

The present paper is an extension of the identification of the predicted terms, including most of the strong quartet terms.

2. *Observational Data.*

The wavelength material used in this work is mostly from the published list of Caroll. Some were taken from the measurements of McQuarie and a few were measured by the authors from their plates.

To provide data likely to be useful in identifying the spectrum of the element at higher stages of ionisation, a study was made of the spark spectrum of the element in air and in vacuum and in hydrogen at different pressures, under varying conditions of excitation. It has been found possible by this method to identify the lines representing successive stages of ionisation, by a careful comparison of the spectra produced under different conditions of pressure and excitation.

3. *Results.*

A rough estimate of the deep-lying inverted ^2D term was first made by Sommerfeld's relativistic doublet law and also by a knowledge of the difference $^3D_3$-$^3D_1$ (d^9s) of Tl IV [1]. This inverted ^2D term should combine with the ^2P term of the regular doublet system. The starting point in the discovery of this inverted ^2D terms ($5d^96s^2$) was given by the identification of the following triplet as $6s^2D$-$7p$ ^2P.

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[1] Phys. Soc. Proc., London, 41, 861, (1929).
Ind. J. Phys., III, 523, (1929).

TABLE II.

	Term value.	$^2D_3$ 177516	(d^9s^2) 18618	$^2D_2$ 158898
$^2P_1$	82748			76150 (1) 1313·20
($d^{10}p$)	5682			
$^2P_2$	77066	100452 (1) 995·5		81834 (0) 1221·98

The choice of this triplet is further supported by the detection of the member 6p $^2P_1$-6s′ $^2D_2$ in the calculated region.

$$6p\ ^2P_1—6s'\,^2D_2=17545 \text{ (cal.)}$$

$$17548 \text{ (obs.)}$$

The difference $^2D_3$-$^2D_2$ = 18618 is very close to the value expected. The inverted ^2D term should combine with the doublet, quartet terms of the group (d^9sp). The combinations identified are given in Table III. It includes also a few combinations due to transitions 6p′⟶7s′.

The super multiplet accompanying the electron transition $5d^96s6p$-$5d^96s6d$, containing about 40 lines in the ultraviolet, has been identified and this confirms the choice of the quartet terms belonging to $5d^96s6p$ configuration. It is given in Table IV.

It will be seen from these tables that the combinations that could not be identified are either very faint or out of range and that the line intensities, term differences and interval ratios are generally speaking, of the right order of magnitude.

There are two lines λλ. 1571·96 and 1215·75 in the required position, having a separation $\Delta\nu = 18639$. It is consequently suggested that they may be classed as

$6s'\ {}^2D_2 - 6d\ {}^2D_2 = 63615$ (4) obs.

63653 cal.

and $6s'\ {}^2D_3 - 6d\ {}^2D_2 = 82254$ (0) obs.

82271 cal.

The triplet λλ. 1457·17, 1221·98 and 1034·74 may be classed as $6p\ {}^2P - 7s'\ {}^2D$ as shown below.

$6p\ {}^2P_2 - 7s'\ {}^2D_3 = 68626$ (3)

13208

${}^2P_2 - \ {}^2D_2 = 81834$ (0)

14809

${}^2P_1 - \ {}^2D_2 = 96643$ (3)

Table V is a catalogue of all the lines classified, together with their wave numbers, intensities and their series designations. The intensities of all the lines in the visible and quartz regions are from our plates.

For the sake of uniformity the term values for the regular doublet terms are those used by McLennan, McLay and Crawford.[1]

The authors wish to express their indebtedness and sincere thanks to Dr. T. Royds, the Director of the Observatory, and to Dr. A. L. Narayan, the Assistant Director, for their continued interest and assistance during the progress of the work.

KODAIKANAL OBSERVATORY,

July 1930.

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[1] Proc. Roy. So ., (A) 125, 50, (1929).

4. *Explanation of Plates.*

Fig. 1 : The spark spectrum of thallium in hydrogen, from λ 4380 to λ 3085.

a, b, c, being spectra taken with different inductances.

Fig. 2 : The spark spectrum of thallium in air for the same region.

TABLE III.

Intercombinations of 6s′ and 7s′ terms with those of 6p′.

$^2D_2$	18618	$^2D_3$	6s′ 7s′ 6p′		$^2D_2$	13208	$^2D_3$
158898		177516			79800		93008
		48383	$^4F_4$	129133			36119 (3)
		(4)		12682			125 cal.
42441		61065	$^4F_3$	116451	36654	(00)	23432 (5)
(2)	18624	(1)		16888	651	cal.	443 cal.
59330		77953	$^4F_2$	99563	19780	(1)	
(1)	18623	(0)			763	cal.	
		59773	$^4D_4$	117743			24728 (4)
		(2)		18574			735 cal.
59723		78347	$^4D_3$	99169			
(3)	18624	(1)		7607			
67336		...	$^4D_2$	91562			
(0)				4308			
71644			$^4D_1$	87254			
(1)							
		79881	$^4P_3$	97685	17865	(1)	
		(1)		12890	885	cal.	
74103		92721	$^4P_2$	84795			
(1)	18618	(00)		-5042			
69061			$^4P_1$	89837			
(00)							

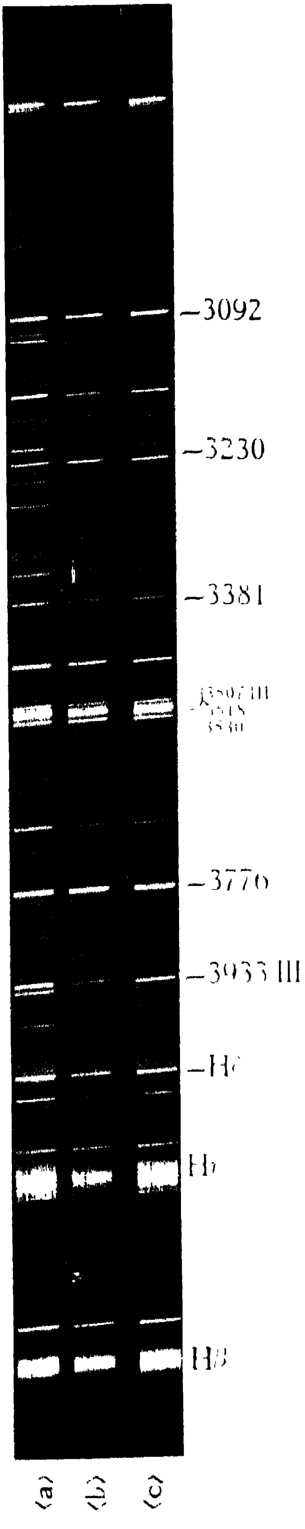

Fig. I

Fig. II

Spark Spectrum of Thallium

TABLE IV.

Super multiplet—Intercombinations of quartet terms of 6p′ and 6d′ configurations.

	6p′	$^4F_5$	7997	$^4F_4$	12682	$^4F_3$	16888	$^4F_2$	$^4D_4$	18574	$^4D_3$	7607	$^4D_2$	4308	$^4D_1$	$^4P_3$	12890	$^4P_2$	-5042	$^4P_1$
6d′		137130		129133		116451		99563	117743		99169		91562		87254	97685		84795		89837
$^4F_5$	96719	40410		32414					21024?											
	8107	(1)	7996	(3)					(1)											
$^4F_4$	88612	48520		40520		27831			[29131]											
	6578	(1δ)	8000	(1)	12689	(5)														
$^4F_3$	84034			45104		32414		15526	[33709]											
	2794			(0)	12690	(3)	16888	(2)												
$^4F_2$	81240					35211		18323			[17929]									
						(1)	16888	(3)												
$^4D_4$	77354	59773		51779		39090			40388		21808?					20331				
	9415	(2)	7994	(1)	12689	(1δ)			(2)	18580	(2)					(5)				
$^4D_3$	67939			61200		48520		31627			31228		23607					16862		
	4580			(7)	12680	(1δ)	16893	(6)			(5)	7621	(4δ)					(4)		
$^4D_2$	63359					53101		36203							23586			21445	?	26478
	3587					(5)	16898	(1δ)							(4)			(1)	5033	(7)
$^4D_1$	59782							39785					31760		27467?					30049
								(4)					(4)	4293	(2)					(4)
$^4P_3$	66060								51685		——					31622		18728		
									(00)							(4δ)	12894	(2)		
$^4P_2$	60986										38287					36699		23810		28839
											(1)					(0)	12889	(4δ)	5029	(4)
$^4P_1$	59930												31627		27336			24870		29897
													(6δ)	4291	(6)			(5)	5027	(4)

NOTE.—The lines 3775·72 and 2763·6 are arc lines and the corresponding faint spark lines probably coincide with the arc lines. The term values of $7s'\,^2D_{32}$ are those determined for the probable combination lines 6p, ^2P–$7s'\,^2D$ and hence the combinations with $7s'\,^2D$ are only tentative. A study of the Zeeman effect of Tl and Pb is now in progress and it is hoped to publish a further account of the analysis in the light of these data.

TABLE V.

λ	ν	I	Designation.	
8001	12495	4	$7p\ ^2P_1-6d\ ^2D_2$	M & A
6439	15526	2	$6p'\ ^4F_2-6d'\ ^4F_3$	
5929	16862	4	$6p'\ ^4P_2-6d'\ ^4D_3$	
5927·8	16865	5	$7p\ ^2P_2-6d\ ^2D_3$	M& A
5697	17548	5	$6p\ ^2P_1-6s'\ ^2D_2$	
5596	17865	1	$6p'\ ^4P_3-7s'\ ^2D_2$	
5499·4	18179	2	$7p\ ^2P_2-6d\ ^2D_2$	M & A
5456	18323	3	$6p'\ ^4F_2-6d'\ ^4F_2$	
5362·40	18643	8	$7s\ ^2S_1-7p\ ^2P_1$	C
5338	18728	2	$6p'\ ^4P_2-6d'\ ^4P_3$	
5086·99	19653	6	$7p\ ^2P_2-8s\ ^2S_1$	C
5054·2	19780	1	$6p'\ ^4F_2-7s'\ ^2D_2$	
4917·3	20331	5	$6p'\ ^4P_3-6d'\ ^4D_4$	
4755·2	21024	1	$6p'\ ^4D_4-6d'\ ^4F_5$	
4661·9	21445	1	$6p'\ ^4P_2-6d'\ ^4D_2$	
4584·3	21808	2	$6p'\ ^4D_3-6d'\ ^4D_4$	
4380·57	22822	5	$7p\ ^2P_2-7d\ ^2D_2$	C
4269·81	23414	10	$7p\ ^2P_2-7d\ ^2D_3$	C
4266·44	23432	5	$6p'\ ^4F_3-7s'\ ^2D_3$	
4234·93	23607	4δ	$6p'\ ^4D_2-6d'\ ^4D_3$	
4198·77	23810	4δ	$6p'\ ^4P_2-6d'\ ^4P_2$	
4185·46	23886	4	$6p'\ ^4D_1-6d'\ ^4D_2$	
4155·75	24056	8	$5f\ ^2F_3-5g\ ^2G$	C
4109·85	24325	10	$7s\ ^2S_1-7p\ ^2P_2$	C
4042·87	24728	4	$6p'\ ^4D_4-7s'\ ^2D_3$	
4019·84	24870	5	$6p'\ ^4P_2-6d'\ ^4P_1$	
3946·02	25335	4	$7p\ ^2P_1-8s\ ^2S_1$	M
3933·05	25418	8	$5f\ ^2F_4-5g\ ^2G$	M
3775·72	26478	7	$6p'\ ^4P_1-6d\ ^4D_2$	
3657·16	27336	6	$6p'\ ^4D_1-6d'\ ^4P_1$	
3639·61	27467	2	$6p\ ^4D_1-6d'\ ^4D_1$	

λ	ν	I	Designation.	
3592·08	27831	5	$6p'\,{}^4F_3-6d'\,{}^4F_4$	
3507·41	28503	9	$7p\,{}^2P_1-7d\,{}^2D_2$	O
3466·53	28839	4	$6p'\,{}^4P_1-6d'\,{}^4P_2$	
3456·34	28924	9	$6d\,{}^2D_3-5f\,{}^2F_4$	M
3343·83	29897	4	$6p'\,{}^4P_1-6d'\,{}^4P_1$	
3327·00	30049	4	$6p'\,{}^4P_1-6d'\,{}^4D_1$	
3300·80	30287	3	$6d\,{}^2D_3-5f\,{}^2F_3$	M
3201·37	31228	5	$6p'\,{}^4D_3-6d'\,{}^4D_3$	
3163·53	31600	6	$6d\,{}^2D_2-5f\,{}^2F_3$	M
3161·40	31622	4δ	$6p'\,{}^4P_3-6d'\,{}^4P_3$	
3060·94	31627	6δ	$\begin{cases}6p'\,{}^4F_2-6d'\,{}^4D_3\\6p'\,{}^4D_2-6d'\,{}^4P_1\end{cases}$	
3147·68	31760	4	$6p'\,{}^4D_2-6d'\,{}^4D_1$	
3084·16	32414	3	$\begin{cases}6p'\,{}^4F_4-6d'\,{}^4F_5\\6p'\,{}^4F_3-6d'\,{}^4F_3\end{cases}$	
2839·18	35211	1	$6p'\,{}^4F_3-6d'\,{}^4F_2$	
2768·6	36119	3δ	$6p'\,{}^4F_4-7s'\,{}^2D_3$	
2761·42	36203	1δ	$6p'\,{}^4F_2-6d'\,{}^4D_2$	
2728·2	36654	00	$6p'\,{}^4F_3-7s'\,{}^2D_2$	
2724·9	36699	0	$6p'\,{}^4P_3-6d'\,{}^4P_2$	
2611·09	38287	1	$6p'\,{}^4D_3-6d'\,{}^4P_2$	
2558·2	39090	1δ	$6p'\,{}^4F_3-6d'\,{}^4D_4$	
2512·78	39785	4	$6p'\,{}^4F_2-6d'\,{}^4D_1$	
2475·24	40388	2	$6p'\,{}^4D_4-6d'\,{}^4D_4$	
2473·90	40410	1	$6p'\,{}^4F_5-6d'\,{}^4F_5$	
2467·9	40520	1	$6p'\,{}^4F_4-6d'\,{}^4F_4$	
2356·2	42441	2	$6s'\,{}^2D_2-6p'\,{}^4F_3$	
2217·1	45104	0δ	$6p'\,{}^4F_4-6d'\,{}^4F_3$	
2066·8	48388	4	$6s'\,{}^2D_3-6p'\,{}^4F_4$	
2061·0	48520	1δ	$\begin{cases}6p'\,{}^4F_5-6d'\,{}^4F_4\\6p'\,{}^4F_3-6d'\,{}^4D_3\end{cases}$	

λ	ν	I	Designation.	
1934·8	51685	00	$6d'\ ^4D_4 - 6d'\ ^4P_3$	
1931·3	51779	1	$6p'\ ^4F_4 - 6d'\ ^4D_4$	
1883·2	53101	5	$6p'\ ^4F_3 - 6d'\ ^4D_2$	
1685·5	59330	1	$6s'\ ^2D_2 - 6p'\ ^4F_2$	
1674·4	59723	3	$6s'\ ^2D_2 - 6p'\ ^4D_3$	
1673·0	59773	2	$\begin{cases} 6s'\ ^2D_3 - 6p'\ ^4D_4 \\ 6p'\ ^4F_5 - 6d'\ ^4D_4 \end{cases}$	
1660·05	60239	8	$6p\ ^2P_2 - 7d\ ^2S_1$	M & A
1637·6	61065	1	$6s'\ ^2D_3 - 6p'\ ^4F_3$	
1634·0	61200	7	$6p'\ ^4F_4 - 6d'\ ^4D_3$	
1571·96	63615	4	$6s'\ ^2D_2 - 6d\ ^2D_2$	
1558·67	64157	8	$6s\ ^2S_1 - 6p\ ^2P_1$	M & A
1506·37	66385	4	$6p\ ^2P_2 - 6d\ ^2D_2$	M & A
1485·1	67336	0	$6s'\ ^2D_2 - 6p'\ ^4D_2$	
1477·14	67699	10	$6p\ ^2P_2 - 6d\ ^2D_3$	M & A
1457·17	68626	3	$6p\ ^2P_2 - 7s'\ ^2D_3$	
1448·0	69061	00	$6s'\ ^2D_2 - 6p'\ ^4P_1$	
1395·80	71644	1	$6s'\ ^2D_2 - 6p'\ ^4D_1$	
1349·47	74103	1	$6s'\ ^2D_2 - 6p'\ ^4P_2$	
1332·36	75055	4	$6p\ ^2P_1 - 7s\ ^2S_1$	C
1313·20	76150	1	$6s'\ ^2D_2 - 7p\ ^2P_1$	
1282·83	77953	0	$6s'\ ^2D_3 - 6p'\ ^4F_2$	
1276·37	78347	1	$6s'\ ^2D_3 - 6p'\ ^4D_3$	
1266·33	78968	10	$6s\ ^2S_1 - 6p\ ^2P_2$	C
1252·65	79831	1	$6s'\ ^2D_3 - 6p'\ ^4P_3$	
1231·57	81197	7	$6p\ ^2P_1 - 6d\ ^2D_2$	C
1221·98	81834	0	$\begin{cases} 6s'\ ^2D_2 - 7p\ ^2P_2 \\ 6p\ ^2P_2 - 7s'\ ^2D_2 \end{cases}$	
1215·75	82254	0	$6s'\ ^2D_3 - 6d\ ^2D_2$	
1078·5	92721	00	$6s'\ ^2D_3 - 6p'\ ^4P_2$	
1034·74	96643	3	$6p\ ^2P_1 - 7s'\ ^2D_2$	
995·5	100452	1	$6s'\ ^2D_3 - 7p\ ^2P_2$	

M = McLennan, McLay and Crawford.
M & A = McLennan etc. and authors.
C = Carroll.

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On the Application of the Ultra-short Wave Method to the Measurement of Small Capacities and Dielectric Constants

BY

D. V. GOGATE, M.Sc., AND D.S. KOTHARI, M.Sc.

Abstract

In a previous paper [1] we had described some experiments on the coupling of two resonant circuits to a triode and from a study of these coupled circuits, a method was suggested of determining the inter-electrode grid-plate capacity of a valve.

The present paper is divided into three sections. The first section deals with the location and measurement of the harmonics that are found to be invariably present along with the ultra-short waves. The conditions necessary for maximum oscillations have been studied.

The general theory of the coupling of two non-resonant circuits to the same valve is discussed in the second section and its application to the measurement of the inter-electrode grid-plate capacity of a valve is described.

In the third section is described the application of the ultra-short-wave method to the determination of the dielectric constants of certain liquids.

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[1] Ind. Jour. Phy., Vol. IV, pt. 5, 1930.

Sec. 1

Short waves were produced by using the oscillatory circuit already described in a previous paper.[1] The valve employed was a French power valve (anode volts up to 600 and fil. volts 5·5). It was also found possible to use two Philip's receiving valves in parallel in place of the valve, the valves 425 giving the best results. Two straight parallel bare eureka wires, S. W. G. No. 16, formed the inductance of the oscillatory circuit. These wires were connected, at one extremity, to the anode and grid pins of the valve and were bridged at the other extremity by a bye-pass condenser. A lecher wire system coupled inductively to the oscillatory circuit was used to measure the wave-length of the short waves produced, a thermo-milliammeter being employed as the detector of the current antinodes. The effect of varying the distance of the negative and of the filament wire 'w' from the grid 'G' was then tried. To do this, the end 'w' of the filament wire was moved along the grid-wire GX (fig. 1) and the current intensity was noted by means of a thermo-milliammeter 'M' coupled inductively to the oscillatory circuit AYXG. It was found that the current intensity was proportional to the

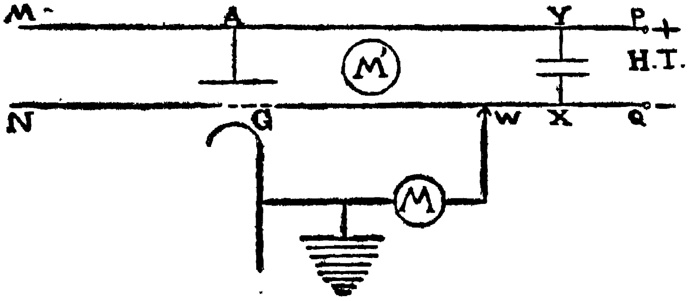

Fig 1.

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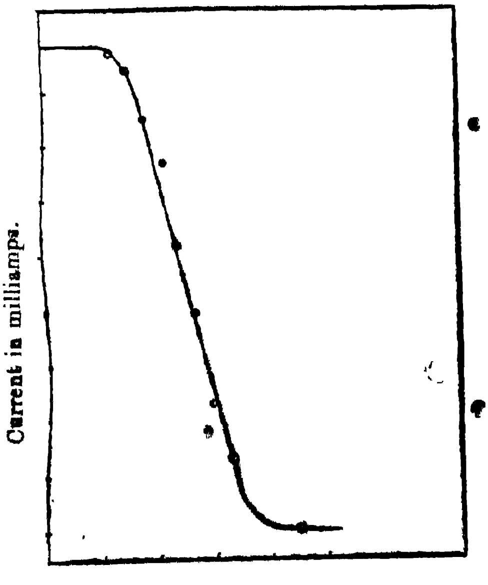
[1] *Loc. cit.*

distance of 'w' from 'G' and became constant at the point 'X' where the grid-wire is joined to the condenser. As 'w' was moved beyond the point 'X' towards 'Q' there was no variation in the current intensity, showing thereby that the latter became constant from the point 'X' onwards. Similarly, when the end 'w' was taken very near 'G' the current fell to zero and remained zero even when 'w' was moved along the grid-wire GN on the other side of 'G'. These facts are represented in fig. 2 where the straight line portion of the curve shows that the current intensity is proportional to the distance of 'w' from 'G' for quite a big range.



Distance from condenser.

Fig 2.

It was also found that the distance of the end 'w' from the grid did not affect in any way the frequency of the waves produced by the oscillatory circuit.

In the production of these ultra-short waves it was only the fundamentals that were studied in the previous papers. The harmonics were however found to be invariably present and their location and measurement were consequently undertaken

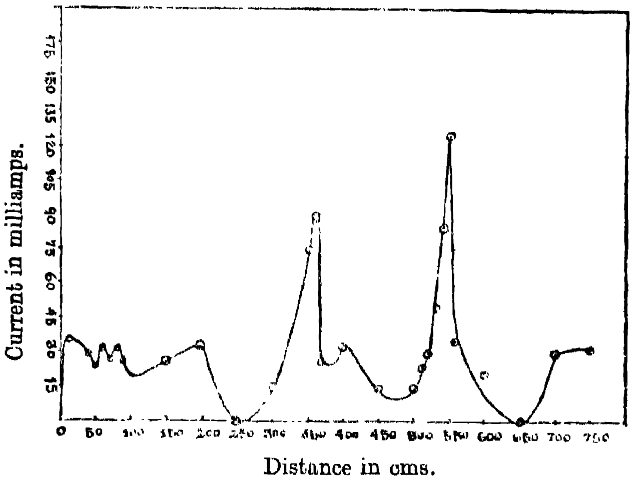


Fig 3 (A).

One method[1] of studying these harmonics, which is quite common, is to connect the thermo-milliammeter to the ends of the lecher wires near the oscillatory circuit. By means of a piece of bare wire, the lecher wire system is then short-circuited at different points along its length and the corresponding changes in the current noted. This has been done and the values of current strength are plotted against the distance of the short circuiting wire from the milliammeter, fig. 3 (A). The graph clearly shows the fundamental at the distance of 550 cms. accompanied by different harmonics.

The harmonics were also studied by another method. The thermo-milliammeter was joined in series with one of the wire 'L' of the lecher system (fig. 4) kept inductively coupled to the oscillatory circuit by a loop passing round a wooden pulley 'P' fixed at a short distance above the circuit. At their extremity, the lecher wires were wound in opposite directions upon a cylindrical ebonite rod and weights were hung from each end of the wires to keep the latter straight. By means of this arrangement it was made possible to measure the current intensity at every point of the lecher-wire system by simply turning the ebonite rod about its axis. At a distance of 550 cms. from the pulley, where maximum current was noted in a preliminary experiment, the lecher wire system was kept short-circuited by a piece of bare wire and then by turning the ebonite rod about its axis, the thermo-milliammeter was moved along the length of the lecher-wires.

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[1] Blake and Ruppersberg, Phy. Rev., Vol. XXXII, (1911).
Blake and Sheard, " " " " (1911).
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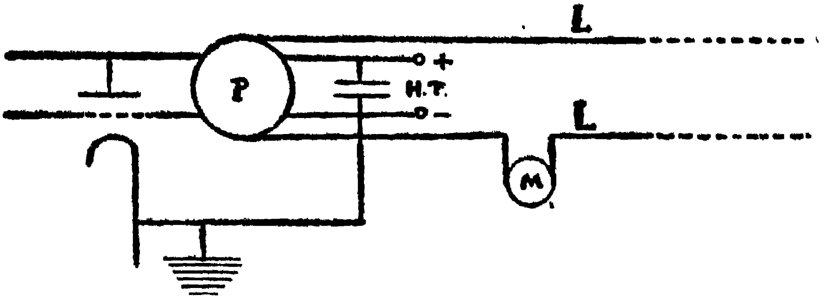

Fig 4.

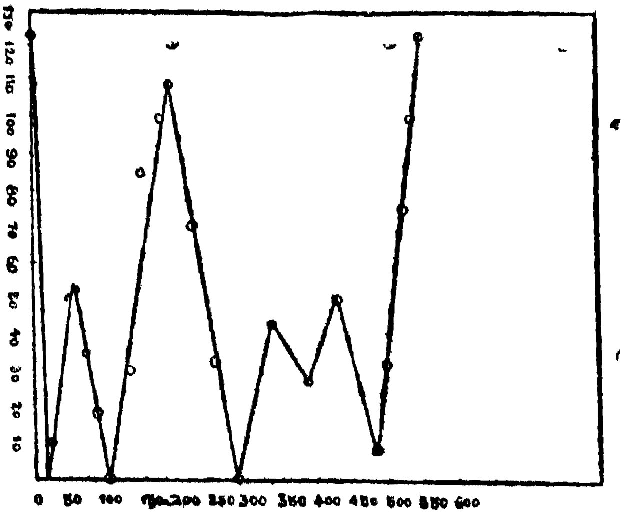

Fig 3 (B)

In this way the current-strength was measured at different points along the lecher-wire system and a graph (fig.

3 B.) was plotted with current against distance from the wooden pulley. This graph shows clearly the presence of two chief antinodes at the distances of 0 and 550 cms. respectively together with the other harmonics that were present.

Sec. 2.

The experiments on the coupling of oscillatory circuits were tried with circuits of different natural frequencies. After measuring the wave-length of the short waves produced with one oscillatory circuit (length of parallel wires 63 cms.) attached to the valve, a second circuit, whose inductance and capacity were different from those of the first circuit, *i.e.*, which was not in resonance with the first circuit, was coupled to the valve on the other side, fig. 5, and the wave-length again measured. The first circuit was now removed and the wave-length determined with only the second circuit present. This process was repeated with circuits of different natural frequencies, the first circuit (length of parallel wires 63 cms.) being kept fixed. In this way different readings were taken and the values of wave-lengths obtained have been given in columns, 3, 4, and 5 of table I.

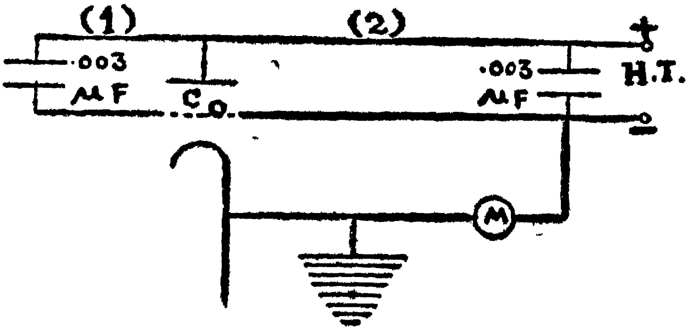

Fig 5.

For a theoretical discussion of the coupled circuits let us represent the oscillatory circuit of fig. 5 by its equivalent simplified diagram (fig. 6).

The C_1 and C_2 of the circuit of fig. 6 are the self capacities of the straight wires forming the inductances of the oscillatory circuits (1) and (2) of fig. 5. L_1 and L_2 are the inductances of the two circuits respectively.

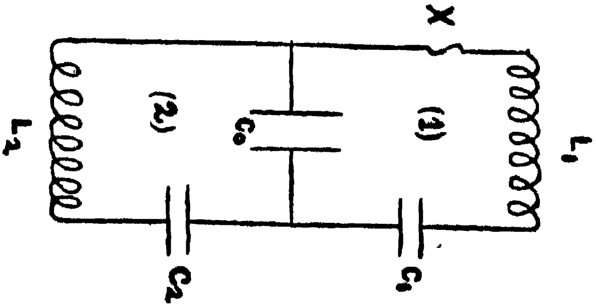

Fig 6.

Let an e. m. f. be supposed to be introduced at X and the total impedance of the two circuits obtained and equated to zero. The solution of the quartic equation in ω thus obtained gives the resonant frequencies of the whole system.

$$\frac{1}{Z_2} = JC_0\omega + \frac{1}{JL_2\omega + \frac{1}{J\omega C_2}} \qquad \ldots \qquad \ldots \qquad (1)$$

where Z_2 is the impedance of the circuit (2)

$$\therefore\ Z_2 = \frac{1-\omega^2 L_2C_2}{JC_0\omega - J\omega^3C_0L_2C_2 + J\omega C_2} \qquad \ldots \qquad \ldots \qquad (2)$$

$$\therefore\ \text{Total impedance} = \frac{1-\omega^2 L_2C_2}{JC_0\omega - J\omega^3C_0L_2C_2 + J\omega C_2} + \frac{1}{JC_1\omega}$$

$$+JL_1\omega = 0 \qquad \ldots \qquad \ldots \qquad (3)$$

$$\because\ \omega^4 - \omega^2\left[\omega^2{}_1 + \omega_2{}^2\right] + \frac{C_1+C_0+C_2}{L_1L_2C_1C_2C_0} = 0 \qquad \ldots \qquad (4)$$

where $$\omega_1^2 = \frac{C_1+C_0}{L_1C_1C_0} \qquad \ldots (5)$$

and $$\omega_2^2 = \frac{C_2+C_0}{L_2C_2C_0} \qquad \ldots (6)$$

ω_1 and ω_2 being the natural frequencies of the two circuits respectively.

On solving this quartic equation,
we have,

$$\omega = \sqrt{\frac{\omega_1^2+\omega_2^2-\sqrt{(\omega_1^2-\omega_2^2)^2+4k^2\omega_1^2\omega_2^2}}{2}} \qquad \ldots (7)$$

where, $$k = \sqrt{\frac{C_1C_2}{(C_1+C_0)(C_2+C_0)}} \qquad \ldots (8).$$

From the values of wave-lengths given in table I, all the frequencies, ω, ω_1 and ω_2 can be calculated and then the value of k can be determined from the above formula.

The self-capacity of the straight wires forming the oscillatory circuits is calculated from the relation[1] :—

$$C = \frac{l}{2 \log_e \frac{2l}{d}} \qquad \ldots (9)$$

where, l = length of the wire,

and d = diameter of the wire.

In this way knowing* the values of C_1, C_2 and k, the value of C_0, the inter-electrode grid-plate capacity of the valve can be calculated from the quadratic equation (8). This has been done in table I where the first two columns give the lengths of the straight wires forming the oscillatory circuits.

---

[1] Electrical Engineer's Data Book, E. B. Wedmore, Vol. III.

Table I.

l_1 in cms.	l_2 in cms.	Wave-length with both circuits present λ in cms.	Wave-length with first osci. circuit present λ_1 in cms.	Wave-length with second osci, circuit present λ_2 in cms.	C_0 in cms.
63	84	458	528	636	7·76
,,	78	448	,,	602	7·35
,,	70	438	,,	582	6·30
,,	66	424	,,	548	5·60
,,	63	416	,,	528	5·90
,,	60	412	,,	512	5·85
,,	55	402	,,	476	6·80
,,	50	386	,,	448	6·35

Mean value of $C_0 = 6·5$ cms.

It will be seen from the above table that the values of C_0 are fairly constant. It may also be noted that the mean value of C_0 obtained by this method agrees fairly well with that given by the resonance method.[1]

Sec. 3.

Measurement of Dielectric Constant.

The method of ultra-short waves was also applied to the measurement of dielectric constant. For this purpose the circuit of fig. 7 was used. The wires BB on the right side are bent at right angles as shown in the fig. The vertical portions of these wires which are equal in length are dipped in a glass vessel in which different liquids whose dielectric constants are to be measured may be filled.

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[1] *Loc, cit.* p. 417 above.

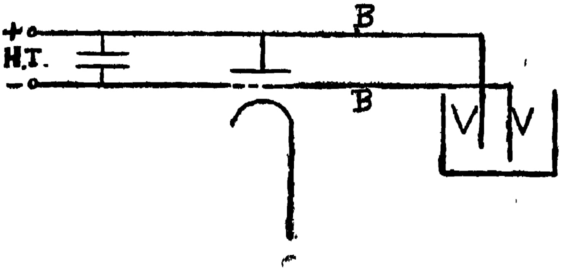

Fig. 7

The principle of the method is to measure the change in wave-length produced by the change in capacity of the vertical portions of the wires when they are dipped in different liquids. From the change in wave-length thus produced, the dielectric constants of the liquids can be determined.

Let k be the capacity of the two parallel vertical portions of the wires in air. Then the wave-length of the oscillatory circuit is given by :

$$\lambda = 2\pi\sqrt{L(C+k)} \qquad \ldots \quad (10)$$

where, L=inductance of the oscillatory circuit,
and C=capacity of the oscillatory circuit.

$$\therefore \quad \lambda^2 = 4\pi^2 L(C+k).$$

Differentiating, we get,

$$2\lambda d\lambda = 4\pi^2 L \, dk$$

$$\text{or} \quad dk = \frac{\lambda d\lambda}{2\pi^2 L} \qquad \ldots \quad (11($$

All the quantities in the right hand expression of equation (11) being known, dk can be calculated.

Now, if l = length of the wire dipped in the liquid,
D=distance between the two dipping wires,
d = diameter of the wire,

then the capacity formed by the two vertical portions of the wires is given by[1] :—

$$k=\frac{\cdot 109l}{\log_{10}\left(\frac{2D}{d}\right)} \qquad \ldots \quad (12)$$

with air as the dielectric.

When the wires are dipped in a liquid of dielectric constant δ, the capacity is given by:[2]—

$$k=\frac{\delta\times\cdot 109l}{\log_{10}\left(\frac{D}{d}\right)} \qquad \ldots \quad (13)$$

$\therefore$ **change in capacity**

$$dk=(\delta-1)\,\frac{\cdot 100l}{\log_{10}(D/d)} \qquad \ldots \quad (14)$$

Substituting the value of dk obtained from equation (11), δ can be calculated.

$$\frac{\lambda d\lambda}{2\pi^2 L}=(\delta-1)\,\frac{\cdot 109l}{\log_{10}(D/d)} \qquad \ldots \quad (15)$$

Length of the wires of the oscillatory circuit 25 cms.
Distance between the two wires of the osci. circuit 8·5 cms.
Diameter of the wire 0·123 cm.
Distance between the two wires dipping 1·0 „
Valves used :—Philips A425 ; Two in parallel.

TABLE II.*

Dielectric	Length dipping	Wave-length	Dielectric Constant
Air	...	603 cms.	...
Kerosene oil	3·9 cms.	615 „	4·06
Petrol	3·3 „	613 „	2·8

* We are indebted to Messrs. Jaichandra and B. D. Pant for these observations.

Fleming's Pocket Book

Calculations :—

(1) Kerosene oil.

$$dk=\frac{\lambda d\lambda}{2\pi^2 L}\,; \qquad \begin{aligned} L&=4l\log_e(2D/d)\\ &=4\times25\times2{\cdot}3\log(17/{\cdot}123)\\ &=492{\cdot}2\text{ cms.}\end{aligned}$$

$$\text{Again, } dk=\frac{l\times{\cdot}109}{\log\frac{2D}{d}}(\delta-1)$$

$$\therefore\quad \delta=4{\cdot}06$$

(2) Petrol.

Similarly, for petrol we get $\delta=2{\cdot}8$.

The experimental procedure can be varied. The R. F. milliammeter is kept fixed on the lecher wires and a graph is plotted between the lengths of the wires VV and the current *in the milliammeter. The wires VV are then dipped in the* liquid and from the change of current in the milliammeter which is kept fixed on the lecher wires, the change in the capacity of the wires VV is noted by means of the graph already plotted. This change in capacity gives immediately the dielectric constant. This procedure gives more accurate results and is better adapted to the study of the temperature variation of the dielectric constant which is to form the subject of a subsequent communication.

Our best thanks are due to Prof. M. N. Saha, F.R.S., for his kind interest in this work.

Boroda College and Allahabad University.

28

Some Abnormal Values of Signal Intensity from Broadcasting Stations.

By

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(*Received for publication, 10th July, 1930.*)

Abstract.

Field strengths from a broadcasting station ($\lambda - 357{\cdot}1$ metres) have been measured at a great circle distance of about 640 kilometres. Observed intensities though varying between wide limits, are found to be several times greater than the values obtained by calculating according to the theoretical propagation equations of Hertz, Austin-Cohen and Fuller. Severe fading is also prevalent on this service. Fading curves on analysing show a variability factor, expressed as a ratio mean square deviation to mean square value of curve, as 40% higher than the variability of a multiray reception curve. Fading is not periodic, the result being the equivalent of the summation of a large number of harmonic vibrations having slightly differing amplitudes and periodicities. Experiments suggest the possibility of change of periodicity during propagation, apparently in the course of reflection at the Heaviside layer.

Signal intensities obtaining around a broadcasting station have from time to time been measured in the case of several important European and American stations. Proceedings, I.R.T. of 1924, 1926, and Journal, I. E. E., 1929 give the contours around New York City and London within a radius of 60-100 kilometres. Unfortunately little information about broadcast field strengths is available for distances of the order of 600-800 kilometres. The subject as such may not be of much interest in European states where broadcasting stations are situated in close proximity to one another and secondly the local station is sufficiently interesting not to drive one to remote foreign stations. In India however conditions are different and wireless stations are few and far between.

The following experiments were undertaken to study the attenuation of broadcast frequencies at such great distances.

Observations were made on the carrier of the Bombay station of the Indian Broadcasting Company, working on λ of 357·1 metres. The special test signal consisted of a long dash of 3 minutes' duration, given immediately after the termination of their evening programmes, at 8-30 p.m. I.S.T. (1,500 G.M.T.)

Intensity measurements were made at this laboratory situated at a great circle distance of 640 km. from the Bombay station. The transmitting aerial is a T supported on two 200 ft. self-supporting lattice steel masts, the physical height of aerial being 150 ft. as given by the authorities with a normal aerial current of about 20 amperes as measured at the base. The effective height assumed for purposes of calculation is 75 ft.

From the application of the well known propagation equations of Hertz, Austin-Cohen, Fuller and others, a field strength of about 600 μV/ meter was anticipated for this aerial power at a distance of 640 km. The papers cited above refer to very much stronger fields. Methods of measurements in this latitudes (13°N) get further complicated on account of having to combat higher noise level prevailing practically throughout the year. From all these considerations, it was thought desirable to construct a super heterodyne type of receiver amplifier. A schematic diagram of the receiver complete with the aerial and a few circuit constants, is given in fig. 1. The intermediate frequency adopted for amplification was that corresponding to 7,000 metres, decided mainly from considerations of available coupling units.

These were high frequency type intervalve transformers tuned to 7,000 metres by ·0003 μF fixed condensers across their primaries. As will be seen from the figure each valve stage is housed in a shielding box of aluminium, thus providing a double shielding side ways.

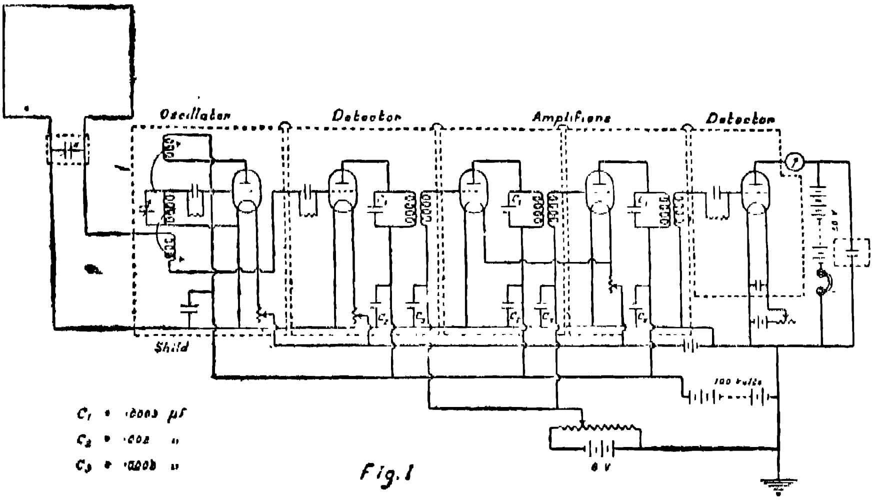

Fig. 1

The aerial consisted of 4 turns of No. 16 s.w.g. copper wire wound on a frame 4 ft. square with a spacing of 2″. It was tuned to resonance at 357·1 metres with a shielded variable condenser.

All observations were made on a sensitive galvanometer in the anode circuit of the last valve which was worked as a balanced detector, with anode and filament supplies independent of the rest of the amplifier. This together with the various bypass condensers incorporated in the set at all high frequency stages rendered the receiver quite stable in operation.

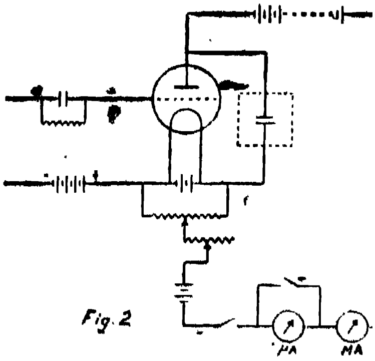

Fig. 2

The experimental procedure was the one usually adopted in signal strength measurements. The receiver was tuned to 357·1 metres and with the aerial cut out, the detector stage was balanced for zero anode current by means of the potentiometer arrangement shown in detail in fig. 2. The aerial was next switched on and the balance restored by minor adjustment of the bias. With the three minutes' dash on, the heterodyne oscillator was adjusted to give a beat of 7,000 metres and the rectified current in the galvanometer noted every half minute. Thus each observation consisted of six readings of $\frac{1}{2}$ minute's interval, the average value being used in all further calculations.

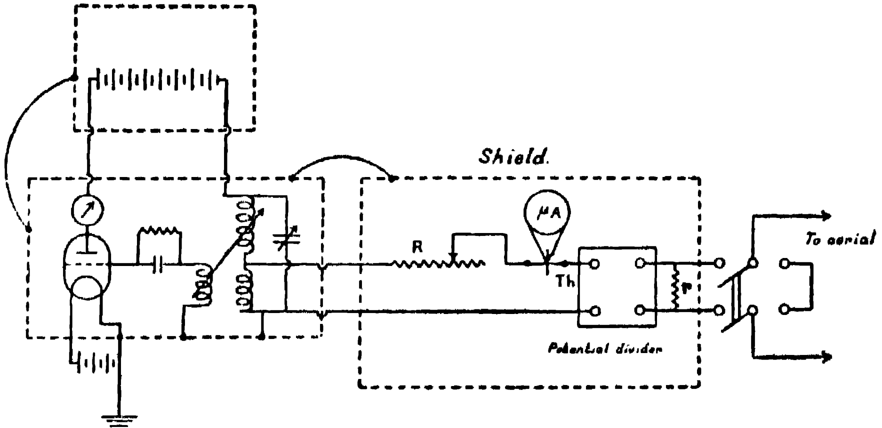

Fig. 3

At the termination of the signal, a small voltage generated by a local oscillator (fig. 3) was introduced into the aerial as shown in the figure. This oscillator was previously set for wave length of 357·1 metres. Its out-put after passing through a high frequency potential divider was attenuated to the required value and taken to the terminals of the one ohm aerial resistancer. The local oscillator with its batteries and the potential divider were all completely shielded. From the attenuator ratio and the current input into the attenuator as measured by the thermo-galvanometer the current and hence the voltage across r can be calculated. Attenuation was adjusted until the detector current obtained from this local signal was about the same as that due to the VUB signals. In actual measurement, a curve was drawn showing the relation between input and the rectified current, the required input voltage corresponding to the signal being then accurately obtained from this curve.

From a knowledge of this voltage and the dimensions of the loop aerial, the field strength is calculated according to the following equations :—

Local emf induced into the aerial = attenuated current × aerial r.

$$e = i\,r.$$

If E = field strength of the signal,

$$\text{aerial voltage} = 2\pi \text{f}.\ \frac{A\,N\,E}{3 \times 10^{12}}$$

This equals the local input voltage ri

$$\therefore\ \text{E}\ \mu\text{V/metre} = \frac{ri \times 3 \times 10^{12}}{2\pi \text{f}.\ A\,N}$$

where i = milliamps.

$A\,N$ = area turns in a square metre.

These observations were made for over four months in the early part of 1929. For purposes of analysis readings have been reduced to the basis of one ampere in the transmitting aerial. The observed extreme intensities were 190 and 30 microvolts per metre per aerial ampere. The mean of the observed figures for the period is 83 μV/metre giving the average field strength as 1,700 μV/metre at a distance of 640 km.

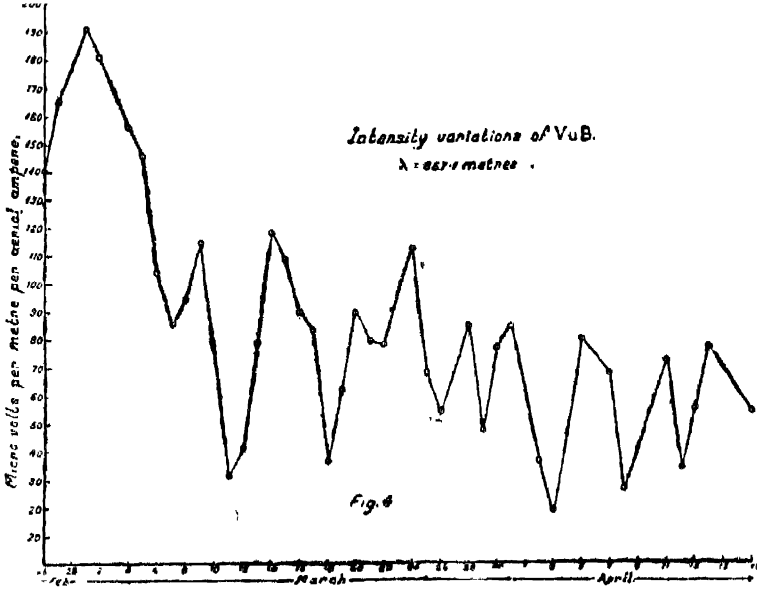

Fig. 4

From a knowledge of the transmitting aerial constants, the following intensities could be expected according to the several attenuation equations :—

Hertz (without attenuation) μV/metre

$$\frac{377 h_s l_s}{\lambda d} = 30{\cdot}1$$

Austin-Cohen—

$$\frac{377 h_s l_s}{\lambda d} \; e \; \frac{-{\cdot}0015 d}{\sqrt{\lambda}} \qquad 24{\cdot}68$$

Fuller—

$$\frac{377 h_s l_s}{\lambda d} \; e \; \frac{-{\cdot}0045 d}{\lambda^{1{\cdot}6}} = 29{\cdot}44$$

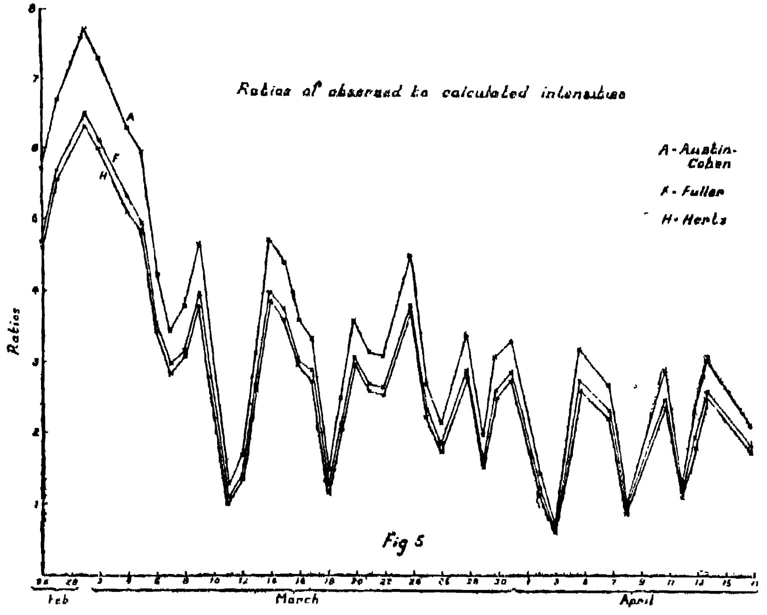

Fig 5

Compared with these figures the observed values are several times bigger, suggesting a condition of negative or anti-attenuation. In fig. 5 have been plotted the ratios of observed values to values calculated according to the above equations. Propagation of wireless signals with negative attenuation has been reported by one or two previous observers. (Proceedings, Cambridge Philosophical Society, Vol. 23, p. 288, 1928 and also Journal, I. E. E., Vol. 67, March, 1927.) These measurements were made at slightly longer wave-lengths and at much closer quarters.

Before attempting an explanation of these unusual figures, a thorough search was made to see if by any chance layout of the wiring of the set could have introduced such a constant error. Even with additional screening of the local oscillator and the leads to the aerial, no change was noticed. The following tentative explanation is offered pending further verification from observations on fading and variation in the direction of arrival of signals and plane of polarisation.

The transmitter is situated practically on an island at sea level. Almost immediately to east and at a distance of about 25 to 35 miles runs a long unbroken stretch of mountains rising to height of 8,000 to 10,000 ft. It would appear that this chain stretching from latitude 22°N to 8°N, (observers latitude 13°N) almost completely eliminates the chances of the direct ground ray being received by eastern districts. In fact the shadow effect seems to be prevalent so far as the ground ray is concerned, reception being possible because of the strong indirect ray. A severe type of fading characteristic of indirect ray reception also prevails on this service. This lends support to the theory that at this distance, the ground ray is absent and signals arrive by reflection from higher altitudes along a few main paths such that at times there is an abnormal increase in strength while at others there is total wipe-out of the signal, due to interference phenomena as in optics.

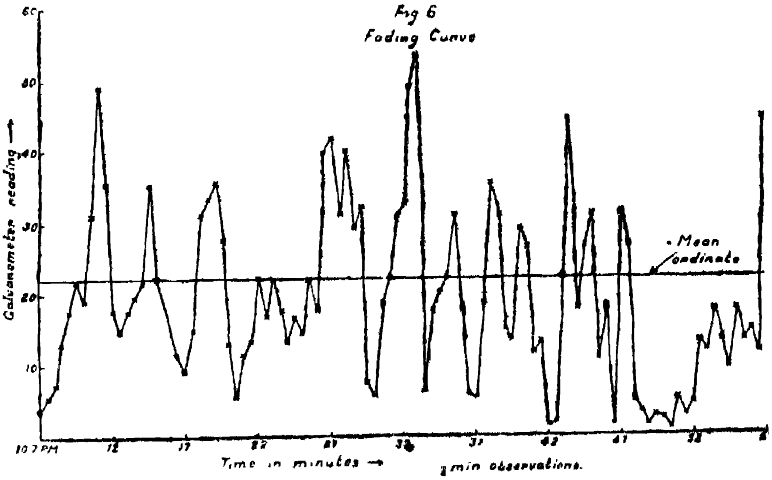

Figure 6 shows a typical fading curve. These observations were made on the superheterodyne set described earlier. Here the detector anode currents observed at half minute intervals are plotted against time of observation. This curve is analysed on the lines suggested by Eckersley (Marconi Review, October, 1928).

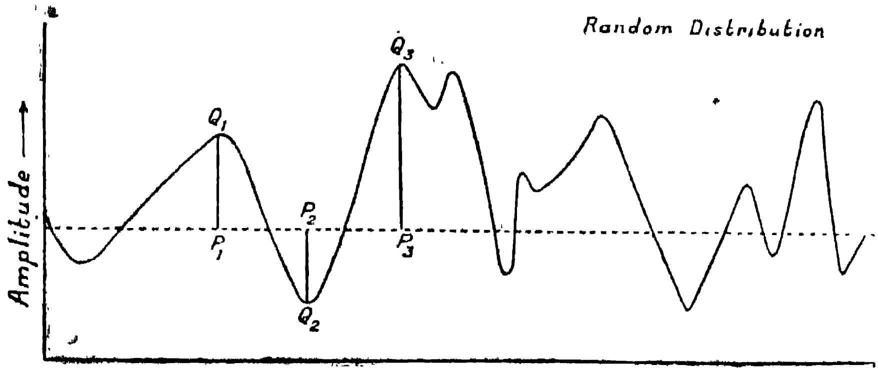

Fig. 6(a)

Any phenomenon which varies with time for example as shown in fig. 6*a* can be considered as a resultant of a number of vectors of random phase difference operating at a given time. At one moment the vectors will add up giving the peaks of the curve and at another oppose one another with a resultant of small amplitude. The mean ordinate however is easily determined. The variability of the phenomenon itself can be expressed as a ratio of the mean square deviation from the mean ordinate to the mean square ordinate. For the figure above, mean of $P_1Q^2_1 + P_2Q_2{}^2 + P_3Q^2_3$......divided by O P^2 is a measure of the variability.

Confining our attention to fading, according to the prevailing theories of propagation, variation of signal intensity between absolute wipe-out of signal and its abnormal strength, may be due to interference between radiations arriving at the receiver by two or more paths of different lengths, and thereby having differences of phase. Assuming for the present that there is no change in the periodicity of the different components the resultant can be expressed (*vide* Theory of Sound, Vol. I, by Lord Rayleigh) as

$$U=\Sigma\, a\cos(wt-e)$$
$$=r\cos(wt-\theta)$$

$$\text{where } r=\left\{(\Sigma a\cos e)^2+(\Sigma a\sin e)^2\right\}^{\frac{1}{2}} \quad\cdots\cdots\cdots(1)$$

$$\text{and } \tan\theta=\frac{\Sigma\, a\sin e}{\Sigma\, a\cos e}$$

For the case of two disturbances with amplitudes a and a_1

$$U=a\cos(wt-e)+a_1\cos(wt-e')$$
$$=r\cos(wt-\theta)$$

$$\text{where } r=\left\{a^2+a_1{}^2+2aa_1\cos(e-e')\right\}^{\frac{1}{2}}$$

$$\text{and } \tan\theta=\frac{a\sin e+a_1\sin e'}{a\cos e+a_1\cos e'}\,.$$

A particular application of this treatment would be where signals arrive by two main paths—the ground ray and the reflected ray. If they are in phase, from the above

(1) $r=(a+a_1)$; $u=(a+a_1)\cos(wt-e)$.

(2) If the phase differences correspond to half a period and an odd multiple of a quarter period r would be $(a-a_1)$

and $\left\{a^2+a_1{}^2\right\}^{\frac{1}{2}}$ respectively.

It should however be noted that the reception curve under these conditions is still a sine function with amplitudes varying between $(a+a_1)$ and $(a-a_1)$. If the signals suffer the same amount of attenuation along the different paths, the amplitude limits would change to 2a and o, without affecting the shape of the reception curve.

Fading curves observed are generally not periodic and rarely show much symmetry about them. A typical curve noticed on the Bombay transmissions is shown in fig. 6 which is very complex indeed.

The two ray theory may be discarded and the problem now considered as purely a statistical one, namely that the observed intensity is the resultant of an infinite number of rays of the same period but of random phase difference. Under such a situation equation No. 1, reduces to

$$r+(\cos e_1+\cos e_2.........)^2+(\sin e_1+\sin e_2.........)^2,$$

with amplitudes assumed as unity for convenience.

For n rays

$$r^2=n+2\sum \cos (e-e_1).$$

For random phase difference the probability is that the sum is as likely to be positive as negative. Consequently the mean value of r^2 is appreciably n. Expressed mathematically, mean square amplitude

$$=\frac{2}{n}\int_0^a e^{-\frac{r^2}{n}}\, r^3\, dr=n.$$

$$\text{Mean square deviation} = \frac{2}{n}\int_0^a e^{-\frac{r^2}{n}}\, r(r-\sqrt{n})^2\, dr$$

$$=n(2-\sqrt{\pi})$$

$$\left.\begin{array}{r}\text{Variability on}\\ \text{multiray basis}\end{array}\right\}\frac{\text{mean square deviation}}{\text{mean square amplitude}}=\frac{n(2-\sqrt{\pi})}{n}\qquad \cdot 228.$$

Variability similarly obtained for a two ray reception appears to be .20. It is therefore interesting to note that on the basis of this analysis, it is difficult to say from an inspection of any fading curve, whether it is a case of two or a large number of rays interfering with one another. The variability of the curve is very nearly the same in either case.

Several fading curves of the Bombay transmissions have been analysed. For fig. 6 mean square intensity is .505 and mean square deviation is .157 giving a variability factor of ·157/·505=·311, about 40% greater than that for multiray interference. It would therefore appear that we have to look for still other factors which tend to increase the unevenness of observed fading curves beyond their limiting variability value of .228.

The premises tacitly assumed in the above calculations are that the amplitudes of individual rays are of the same magnitude as also their periods. One cannot see any *a priori* reason for such a probability. It is more likely that the rays suffer different amounts of attenuation along the different routes. Secondly, in the course of reflection a change in periodicity *may* also take place. The resultant of two harmonic motions of differing amplitudes and periods can be expressed as follows:—

$$U=a\cos(wt-c)+a\cos(wt_2-e')$$

This no longer represents a sine function. The value of U is non-recurring except when the periods of the two variations are in the ratio of two whole numbers, the period of recurrence being the least common multiple of individual periods. The above fading curve is non-recurring. It may therefore perhaps be postulated that the type of fading described shows a preponderance of multiray reception accompanied by minute changes both in frequency and amplitude.

The writers wish to take this opportunity to thank the wireless branch (Posts and Telegraphs Dept., Govt. of India) and the late Indian Broadcasting Co., Ltd., who kindly arranged for the special test transmissions.

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29

The Dielectric Polarisation of Liquid Mixtures.

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Introduction.

The molecular polarisation of a substance in which the molecules are free to assume a perfectly random orientation can be expressed by the equation $P=\frac{\epsilon-1}{\epsilon+2}\cdot\frac{M}{\rho}$ where ϵ is the dielectric constant of the substance, M its molecular weight and ρ its density. Debye theory[1] introduces the molecular polarisation in the form $P=A+\frac{B}{T}$ where A and B are two constants for the dielectric; A is equal to molecular refraction $\frac{n^2-1}{n^2+2}\cdot\frac{M}{\rho}$ extrapolated to infinite wavelength and B is equal to $\frac{4\pi N}{9K}\mu^2$ in which N=Avogadro number, K=Boltzmann gas constant and μ=permanent electric moment of a single molecule forming a doublet. A includes the polarisation due to electric shifts induced in the molecule while B includes the polarisation due to doublet orientation caused by external field. In the case of gases the molecules are most free to move and experimental investigations[1] show that the expression $P = A + \frac{B}{T}$ represents admirably the temperature variation of dielectric constants of dipole gases. In the case of solids, however, the molecules are rigidly bound and therefore unable to orient themselves in an applied field with the result that B vanishes in this case. But as A, the extrapolated value of molecular refraction, does not account for the polarisation due to shifts of atoms or radicals induced in the molecules, P does not equal A. Errara[2] has indeed found out the polarisation P of a number of substances in the solid state showing that P differs from A calculated from optical data by definite constants depending on their infra-red frequencies. Thus $P - A$ is constant for solids, whereas it is an inverse function of temperature in the case of gases. But in the case of liquids, the molecules are neither rigidly bound nor perfectly free and thus $P - A$ becomes an odd function of temperatures which the simple theory is quite inadequate to explain. In the case of alcohols,[3] the curves of P versus $\frac{1}{T}$ give a negative slope suggesting an imaginary moment of the molecule. The failure of Debye theory in the case of polar liquids is generally attributed to association between molecules themselves. This association is presumably a function of concentration and temperature of the liquid. The effect of such association is generally to form molecular complexes so as to diminish the average effective moment just as in grouping of line magnets in ordinary iron pieces. To study the changes of association, the usual method is to dissolve the polar liquid in a non-polar solvent and find the molecular polarisation of the solution at different concentrations and temperatures. P is calculated from the equation $M = M_1C_1 + M_2C_2$ where M_1, M_2 are molecular weight and C_1, C_2 are the molecular fraction concentrations of the solvent and the solute respectively. If the polarisation of the solvent and the solute be denoted by P_1 and P_2, P can be expressed as $P_1C_1 + P_2C_2$ in which P_1 is constant for the nonpolar solvent. Thus P_2 can be calculated from the expression $\frac{\epsilon-1}{\epsilon+2}.\frac{M_1C_1+M_2C_2}{\rho} = P_1C_1 + P_2C_2$ and plotted against concentration C_2 in a curve which would reveal the nature of association in the liquid. Investigations[1] in this direction clearly point out that the effect of association markedly diminishes with the lowering of concentration, and Debye has suggested that the zero-concentration intercepts of such curves would give the molecular polarisation of the solute in the unassociated state. This is based upon the assumption that the association vanishes towards zero concentration. It may therefore, be conjectured that Debye theory might hold for these extrapolated values of P_2 at different temperatures. To test the theory, data for low concentrations must be numerous and reliable so as to give well-defined intercepts and measurements should be carried on at several temperatures, but unfortunately few liquids have been tested from this stand-point. The present work is undertaken to study the nature of association in the case of some simple substituted benzene compounds, to check the zero-concentration intercepts against Debye theory and to find out the moments of the liquids. From its spherical structure, carbon-tetrachloride seems to be the most nonpolar substance, so that this liquid was taken as the solvent and measurements were carried out mostly with low concentration and at several temperatures.

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[1] Marx, Handbuch der Radiologie, 6, 614-619 (1925).

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[1] Zahn, Phys. Rev., 24, 400 (1924). Jona, Physik, Z., 20, 14 (1919). Smyth and Zahn, Journ. Am. Chem. Soc., 47, 2501 (1925). Sanger, Physik, Z., 27, 556, (1926), 28, 455 (1927).

[2] Errara, Physik, Z., 27, 764 (1926).

[3] Marx, Handbuch der Radiologie, 6. 630 (1925).

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[1] Marx, Handbuch der Radiologie, 6, 630 (1925).
L. Lange, Zeits. f. Physik, 33, 169-182 (1925).
Smyth and Morgan, Journ. Am. Chem. Soc., 50, 1547 (1928).

Experimental Procedure.[1]

The dielectric constant of the mixtures was measured by a Heterodyne arrangement usually adopted for measurements on gases.[2] The method is too sensitive for the present purpose, but for low concentration $P-P_1C_1$ is very small and a slight error in the dielectric constant becomes enormously magnified in the process of calculation, so that this necessitates a very accurate determination of dielectric constant at low concentrations. The apparatus consisted of two similar reaction circuits A and B (fig. 1) oscillating with high frequency.

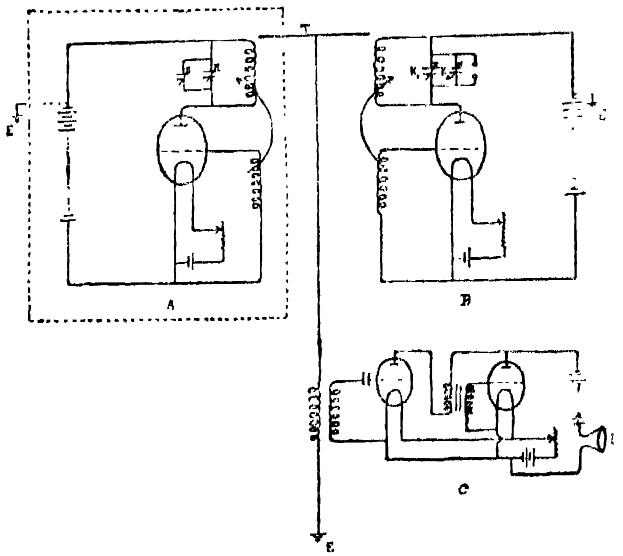

Fig. 1—Diagram of apparatus.

The oscillating valves were of Mullard P. M 4 type operated with 100 volts on the plate and 4 volts on the filament current of 12 amperes and a plate current of about

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[1] The experimental procedure was exactly the same as described in a paper on "The dielectric constant of nitrobenzene" by Mr. N. N. Pal of this laboratory. This has recently been sent for publication, and the details are given here only because that paper is not yet published.

[2] C. T. Zahn, *loc. cit.*

10 milliamperes. The circuits were shielded from each other and run from independent batteries. The oscillation of A was maintained constant at 400 kilocycles generating waves of $\lambda = 750$ m. while that of B was adjusted by variable condensers K_1 and K_2. The high frequency oscillations fell on the aerial T and was amplified in another circuit C to obtain the beat tone in the loud speaker L. By adjusting K_1, K_2 this beat tone was maintained in unison with an electrically driven fork not shown in the figure. Thus the frequency of B could always be brought to a fixed value. The liquid in question was introduced in a condenser which was joined in parallel with K_1 and K_2. These were Radio-precision condensers of which K_1 read up to 3 m. mf. and K_2 a vernier condenser, read up to 0·4 m. mf. The importance of accurately calibrating these condensers has been pointed out by Zahn and others[1] in their measurements on gases. In the present case calibration was performed in the following manner. A and B were identical circuits, so that the beat tone in the loud speaker could be adjusted to unison with the fork either by varying the capacities of K_1 and K_2 in circuit B or by varying the capacities of the corresponding condensers in the circuit A.

To calibrate K_1, unison with the fork was initially obtained with a particular value of K_1; next an air condenser similar to K_2 was introduced in parallel with K_1 and K_2 and unison re-established by varying condensers in the circuit A. Now the air condenser was removed from the circuit and unison was established again by varying K_1 and K_2. It would not be out of place to mention here that K_1 should be calibrated independently of K_2 so that K_2 should be changed as slightly as possible. Thus by alternately introducing and removing the air condenser, K_1 was calibrated throughout the scale. The readings of K_1 were read from a big circular scale of 50 cm.

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[1] *loc.cit.*
E. O. Fritts, Phys. Rev., 23, 345 (1924).

diameter with the help of a long glass pointer attached to the condenser. This magnified the scale sufficiently and provided an easy means of setting the condenser truly to some particular value. K_2 was calibrated in a similar manner, but this time instead of the air condenser the change of capacity required to obtain unison with the fork on both sides of the high frequency silence position was taken as the step and the unison was obtained by alternately changing K_2 and the corresponding condenser in the circuit A, all the other condensers remaining fixed. Next the values of the smallest divisions of K_1 and K_2 were compared at different positions of K_1 and the ratio of the two corrected scales found out. These capacities were shielded from external influences by earthed tin foils.

The method of operation in the case of dielectric constant measurement was to obtain the high frequency beat tone initially in unison with the fork and to re-establish unison when the measuring condenser was introduced. This was done by varying K_1 and K_2, the other circuit remaining unaltered. Since the frequency remained constant the change of capacity was only to compensate for placing the measuring condenser in parallel with K_1 and K_2; thus the difference of condenser-readings gave the capacity of the liquid condenser. It was observed that even when the batteries were in good condition the valves took some time to reach a steady state; the circuits were therefore initially run for about half an hour to obtain steady unison before measurements could be started.

The measuring condenser consisted of two concentric gold-plated brass cylinders A and B mounted in a glass bulb as shown in fig. 2. The inside cylinder was closed at both ends and a gold-plated brass rod attached to the upper end was fitted in the glass capillary and fused there by means of a platinum wire welded to the rod. The outer cylinder was open at both ends and held tightly by two rectangular

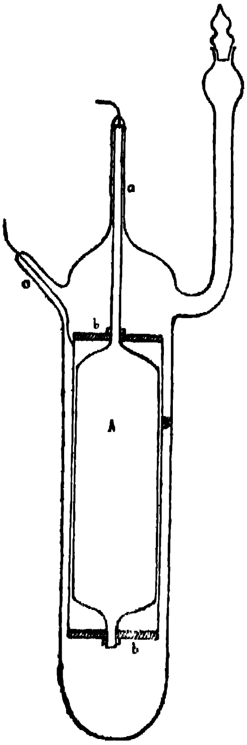


Fig. 2.

glass pieces 'b','b' with screws attached to the centre rod and a platinum wire welded to it was fused to the small side tube 'c'. The cylinders were fixed at 1 mm. apart and the air-capacity of the condenser was 42 m.m.f. This was found by perfectly drying the glass bulb and finding the capacity of the dry condenser. The capacity of the condenser was then found with the liquid inside it and the ratio of the two values gave the dielectric constant of the liquid. But the capacity of the measuring condenser consisted of two parts ; one was the fixed capacity due to the leads and insulation which did not vary with the dielectric constant of the liquid and the other was the capacity between the cylinders which was directly proportional to the dielectric constant. To eliminate the first part an imitation lead was prepared and mounted in a similar glass bulb and its capacity was determined in the same position as in the experiment proper. Several readings gave consistent results and this correction was applied to all subsequent capacity measurements. The air-capacity of the measuring condenser was examined for temperature variation but no appreciable change was observed, and its value was checked from time to time. In the case of liquid measurements, the bulb was dried perfectly and the liquid was introduced to fill the capillary and the side-tube completely.

The glass bulb containing the measuring condenser was clamped by a wooden stand in a bath of distilled water for which a glass thermostat 10″ in diam. and 12″ high was employed. This was jacketed with asbestos sheet and cotton, and the temperature was maintained uniform by means of a glass stirrer and recorded by a mercury thermomenter reading up to ·1°C. It was observed that the level of water in the bath had some influence on capacity measurements ; for this reason the same level was always maintained, and the correction mentioned above was found for the same position of the water level. All metal parts were avoided and the capacities were changed with long glass rods from a distance. Measurements were made at intervals of 10°C and the readings were noted when the beat tone remained steady for about ten minutes confirming temperature equilibrium within the liquid in question.

The density of the mixtures was determined by a special form of density bottle shown in fig. 3. This consisted of a glass bulb A of 30 cc. capacity with a stoppered overflow bulb B with good ground glass joint at 'a'. The bulb with B attached to it tightly was filled with the liquid in question with excess of liquid in the bulb B. This was then hung by a thread and immersed in the water bath and when the temperature equilibrium was established the level of the liquid was adjusted to a definite scratch 'b' by introducing small capillary tubes in B. The stopper C was then fitted tightly and the vessel allowed to come to room temperature before weights were taken. The density and capacity measurements were carried out simultaneously. The bottle was calibrated from standard density values for water and has been found very convenient for volatile liquids.

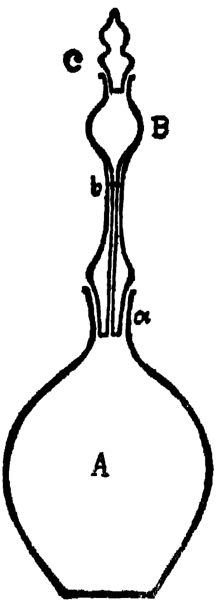


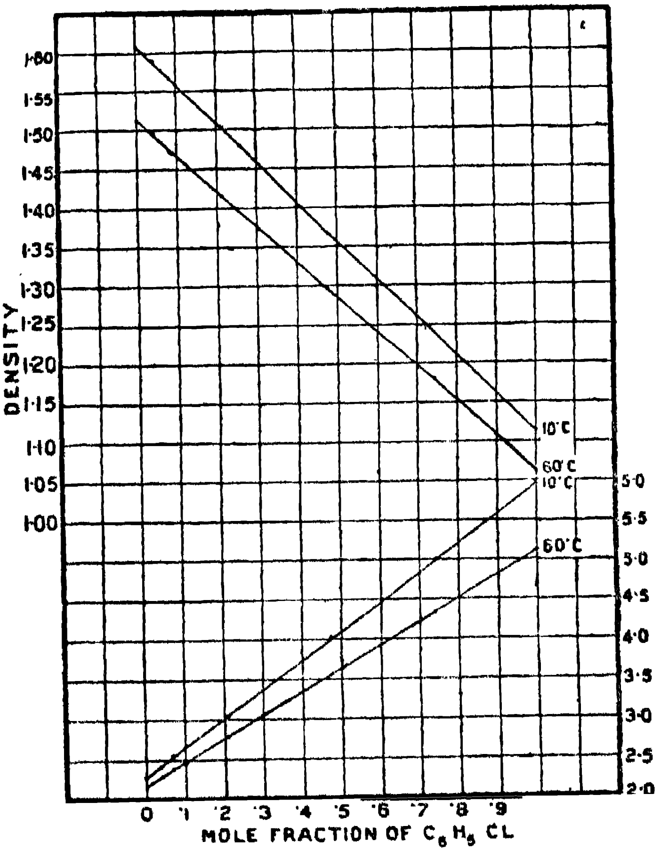
Fig. 3.

The materials used were Merck's carbon tetrachloride redistilled over calcium chloride and Kahlbaum's chlorobenzene and bromobenzene specially prepared for refractive index measurement. The density values were checked and found to agree with tabular results in Landolt "Tabellen". The liquids were accurately weighed in stoppered bottles and great care was exercised in making up the solution to avoid evaporation in the process of mixing and transfering. The same samples were used throughout the measurement.

Data and Results.

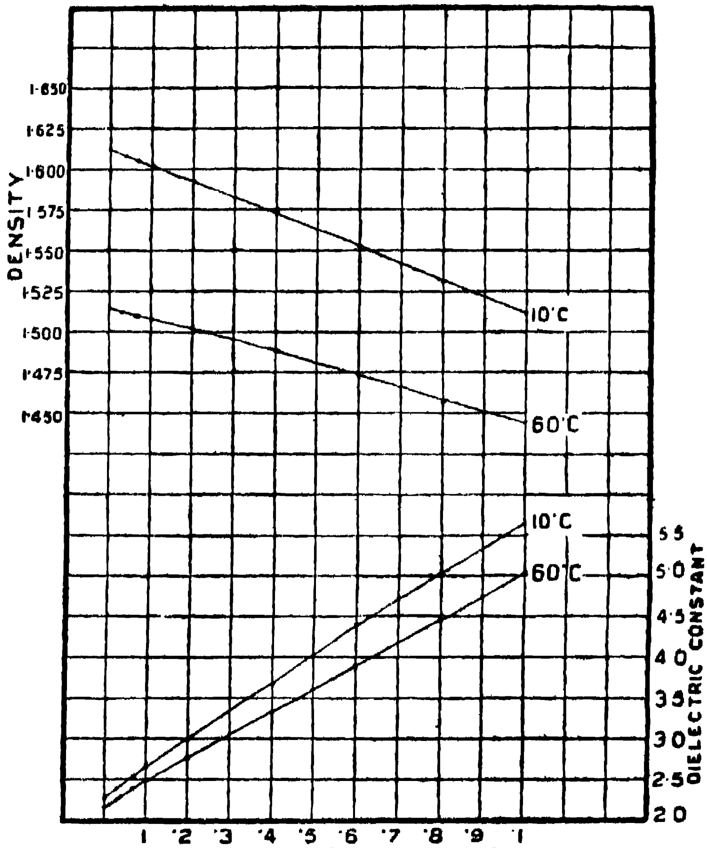
Several solutions of chlorobenzene and bromobenzene in carbon tetrachloride were employed, of which about eight were low concentration solutions for each, and their dielectric constants and densities were determined at temperatures ranging from 10° to 60°C. The results were collected in tables I and II and the dielectric constants and densities were for comparison plotted against molecular concentration at 10° and 60°C (figs. 4 and 5). P was then calculated and P_2 found out.

Fig. 4.



DIELECTRIC CONSTANTS AND DENSITIES OF CHLOROBENZENE CARBON TETRACHLORIDE MIXTURE AT 10° AND 60°C

Fig. 5.



DIELECTRIC CONSTANT AND DENSITIES OF BROMOBENZENE CARBON TETRACHLORIDE MIXTURES AT 10° AND 60°C

These results were collected in tables III and IV, and the values of P were plotted against concentration in figs. 6 and 7. Something should however be said regarding the calculation of P_2. Carbon tetrachloride has theoretically no moment, so that it should give a constant molecular polarisation; but as has been pointed out by Graffunder,[1] Grützmacher[2] and others in the case of benzene, the molecular polarisation of carbon tetrachloride increases slightly with temperature.

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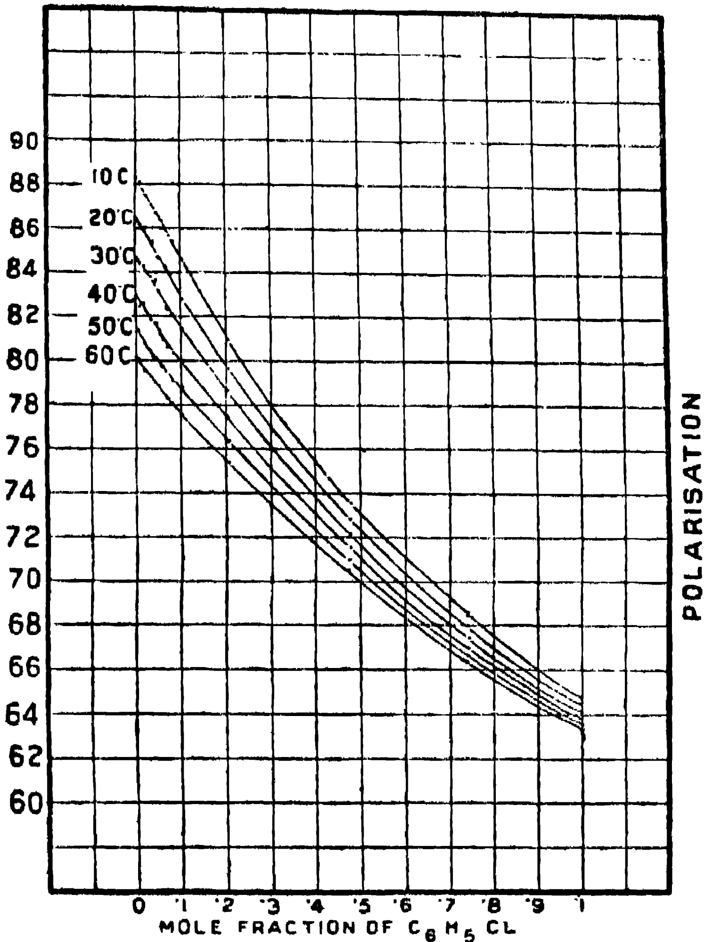
[1] W. Graffunder, Ann. d. Physik, 70, 232 (1923).

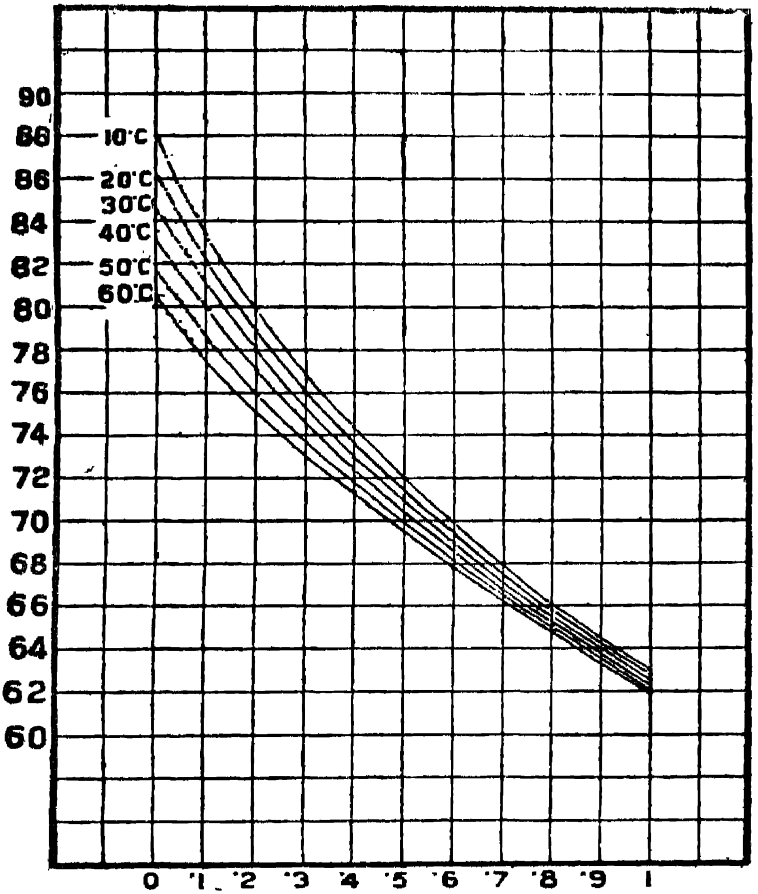
[2] M. Grützmacher, Zeits. f. Physik, 28, 349 (1924).

Fig. 6.



MOLE FRACTION OF C_6H_5Cl
POLARISATION (P) OF CHLOROBENZENE IN CARBONTETRA CHLORIDE SOLUTION AT DIFFERENT TEMPARATURES

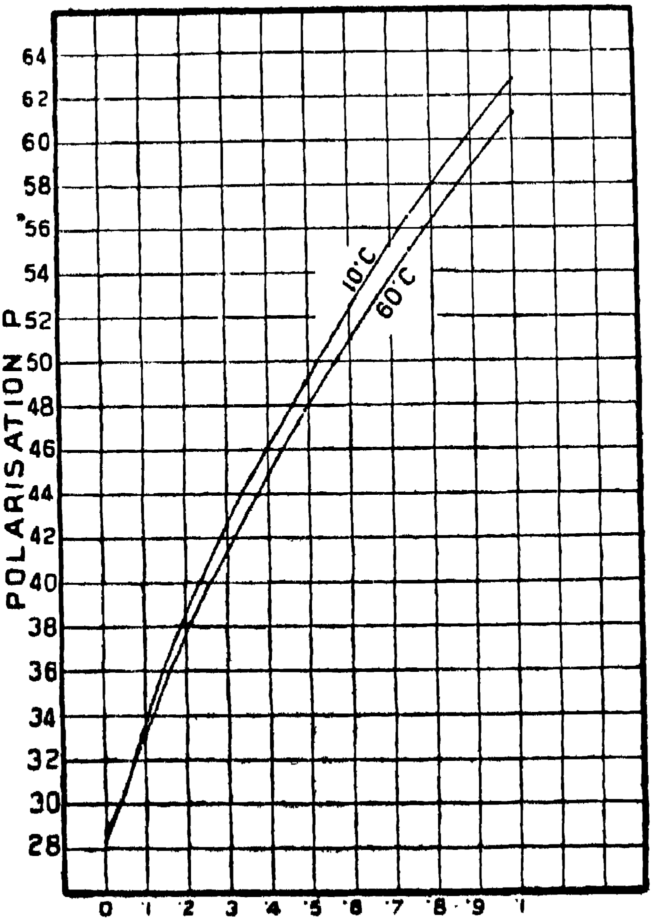
Fig. 7.



POLARISATION (P_2) OF BROMOBENZENE IN CARBON TETRACHLORIDE SOLUTIONS AT DIFFERENT TEMPARATURES.

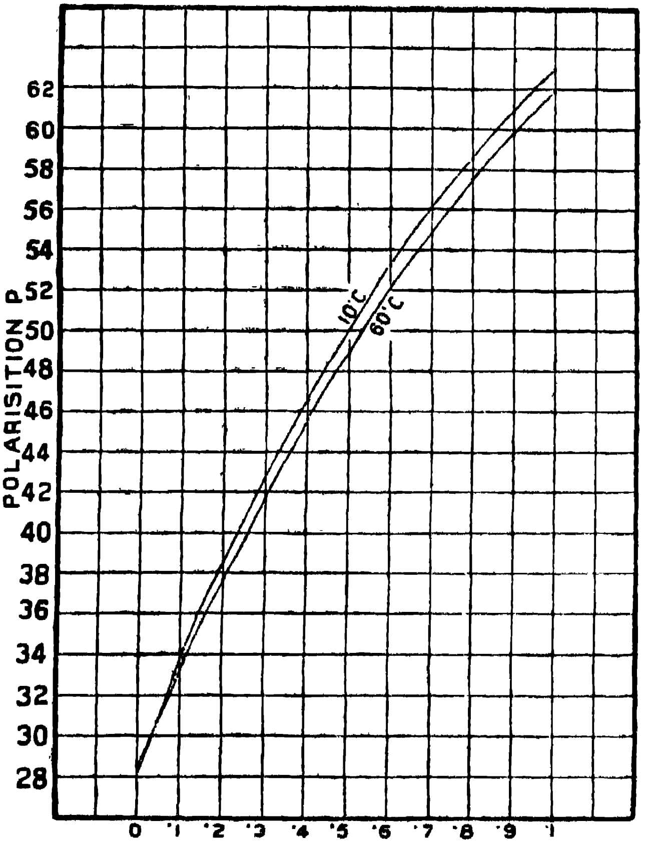
This would enormously affect the value of P_2 at low concentration; so to avoid unnecessary errors P_2 was calculated from the particular values of P_1 obtained at the corresponding temperatures and the same samples were always used. This procedure also avoids any effect of slight impurity present in the solvent. P_2 was then plotted against C_2 (figs. 8 and 9) and the curves were extrapolated to obtain the zero concentration intercepts. The low concentration points show a little diver-

Fig, 8.



POLARISATION (P) OF CHLOROBENZENE-CARBONTETRA CHLORIDE MIXTURES AT 10° AND 60° C

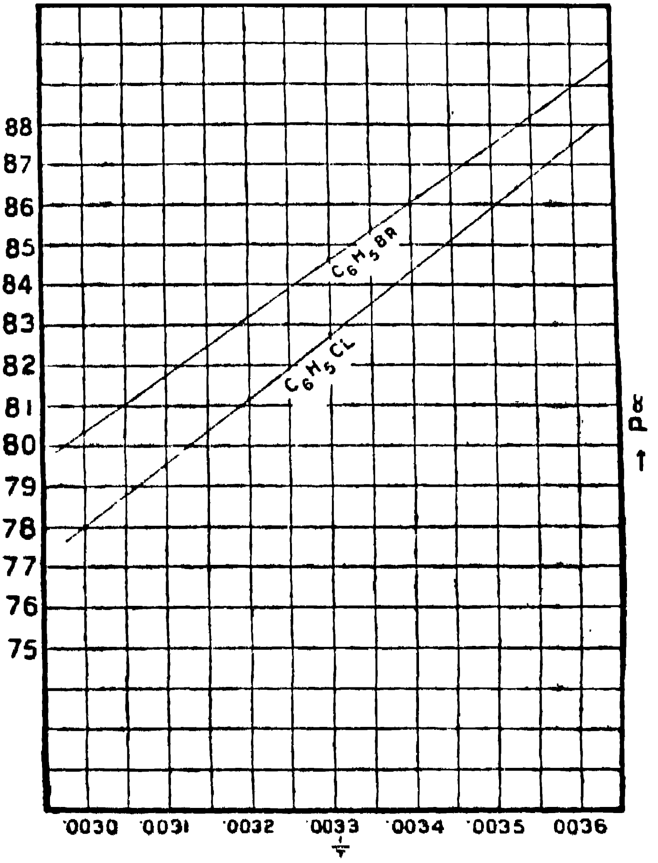
Fig 9.



POLARISATION (P) OF BROMOBENZENE-CARBON TETRACHLORIDE MIXTURES AT 10° AND 60° C.

gence, but the average direction cannot be mistaken and the intercepts were well-defined. To test Debye theory the intercepts P_a were plotted against $\frac{1}{T}$ (fig. 10).

Fig. 10.



VARIATION OF P_α WITH $\frac{1}{T}$ FOR CHLOROBENZENE AND BROMOBENZENE SOLUTIONS IN CARBON TETRACHLORIDE

Discussion of results.

It would be observed from the curves with P_2 versus C_2 that the substances show the simplest type of association. The curves are quite regular and association increases with concentration and temperature as was expected from theory. Curves with P_a and $\frac{1}{T}$ do not show any systematic curvature even when drawn on a big graph paper but practically give straight lines standing strongly in favour of Debye theory. The moments and the optical data were then calculated from these curves. The values of A come out to be nearly equal to the molecular refraction term extrapolated to infinite wavelength and are shown in table V. Of course such a low range of temperature as adopted here does not admit of extrapolation to a very high temperature; but the practically constant values of B obtained theoretically from different values of P_a indicate that the moment would be very nearly the same. Most of the investigators in this line obtained the curves of P_2 *versus* C_2 with ordinary concentrations and extrapolated them to zero concentration but it has been observed that extrapolation from ordinary concentration is not at all reliable; besides they calculated the moment on the assumption of the validity of Debye equation $P=A+\frac{B}{T}$ holding at zero concentration. But the method adopted here is quite independent and satisfactory. The values tabulated above agree with the values obtained by Hojendahl and Smyth and Morgan within limits of experimental error. As regards the experimental method it has been observed that P and P_1C_1 become so nearly equal at low concentration that their difference is not so reliable below ·03 conc. unless the dielectric data can be obtained up to four decimal figures, and an error of ·05% in the dielectric value there involves an error of 1% in the value of P_2. For this reason smooth curves were drawn with dielectric constants and densities plotted against concentration and the values for calculating P were taken from these curves. Small bubbles were observed to form in the condenser at high temperatures between 50° to 60° C, but the values of dielectric constants remained practically unaltered when all the measurements were repeated during cooling. As regards density measurements, low temperatures gave some trouble, for when the liquid expanded at room temperature air tried to escape through the side of the stopper C along with some vapour. This difficulty was got over by tightly pressing the glass stopper occasionally and the error in any case did not exceed ·02%. Work with iodobenzene is in progress and then we shall be in a position to study in a generalised manner the nature of the curves of P_2 *versus* C_2 for these simple substituted compounds. In conclusion we express our heartfelt thanks to Prof. S. N. Bose for his kind guidance aud helpful interest throughout the work.

Summary.

Dielectric constants of solutions of chlorobenzene and bromobenzene in carbon tetrachloride have been accurately measured by the Heterodyne method and their densities determined by a special form of density bottle.

The molecular polarisation was calculated and curves were drawn with partial polarisation and concentration of the polar liquids. The zero concentration intercepts gave values which satisfy Debye formula $P=A+\frac{B}{T}$ The moments of these liquids were calculated. It was observed that association increases with concentration and temperature.

TABLE I.

Dielectric constants and densities of chlorobenzene carbon tetrachloride solutions at different temperatures, the upper value being the dielectric constant and the lower one the density.

Molar fraction of C_6H_5Ce	TEMPERATURES.					
	1 0°C	20°C	30°C	40°C	50°C	60°C
0	2·260	2·241	2·223	2·205	2·186	2·167
	1·6130	1·5940	1·5748	1·5551	1·5356	1·5156
·009201	2·294	2·273	2·253	2·233	2·213	2·192
	1·6091	1·5899	1·5705	1·5506	1·5314	1·5108
·02113	2·337	2·314	2·292	2·271	2·247	2·226
	1·6027	1·5838	1·5644	1·5451	1·5255	1·5062
·03690	2·393	2·368	2·343	2·318	2·293	2·270
	1·5940	1·5755	1·5565	1·5371	1·5180	1·4984
·04258	2·414	2·388	2·362	2·336	2·310	2·285
	1·5915	1·5725	1·5536	1·5343	1·5151	1·4959
·05796	2·470	2·440	2·412	2·382	2·354	2·329
	1·5828	1·5614	1·5460	1·5261	1·5076	1·4886
·07562	2·535	2·503	2·469	2·437	2·407	2·378
	1·5745	1·5560	1·5374	1·5184	1·4992	1·4806
·08465	2·567	2·533	2·498	2·464	2·432	2·403
	1·5685	1·5508	1·5325	1·5133	1·4946	1·4758
·1055	2·641	2 604	2·568	2·532	2·498	2·463
	1·5580	1·5409	1·5227	1·5042	1·4855	1·4667
·2149	3·040	2·982	2·928	2·876	2·824	2·774
	1·5031	1·4859	1·4686	1·4513	1·4338	1·4162
·4810	4·021	3·919	3·821	3·732	3·650	3·575
	1·3696	1·3548	1·3400	1·3246	1·3100	1·2949
·7427	5·003	4·864	4·728	4·594	4·478	4·363
	1·2445	1·2319	1·2188	1·2057	1·1932	1·1803
1	5·956	5·778	5·602	5·437	5·290	5·154
	1·1170	1·1065	1·0955	1·0849	11·074	1·0634

TABLE II.

Dielectric constants and densities of bromobenzene-carbontetrachloride solutions at different temperatures, the upper value being the dielectric constant and the lower one density.

Molar fraction of C_6H_5Br.	Temperatures.					
	10°C	20°C	30°C	40°C	50°C	60°C
0	2·260	2·241	2·223	2·205	2·186	2·167
	1·6130	1·5940	1·5748	1·5551	1·5356	1·5156
·010014	2·297	2·276	2·256	2·237	2·216	2·19
	1·6122	1·5932	1·5738	1·5543	1·5347	1·5151
·02049	2·335	2·312	2·291	2·269	2·247	2·225
	1·6112	1·5920	1·5730	1·5535	1·5340	1·5138
·04110	2·410	2·384	2·359	2·335	2·310	2·285
	1·6100	1·5905	1·5710	1·5518	1·5328	1·5130
·04893	2·438	2·411	2·385	2·359	2·333	2·360
	1·6090	1·5900	1·5705	1·5512	1·5320	1·5124
·06420	2·493	2·464	2·436	2·408	2·379	2·352
	1·6075	1·5888	1·5692	1·5500	1·5310	1·5116
·07837	2·545	2·514	2·484	2·453	2·422	2·393
	1·6058	1·5877	1·5680	1·5488	1·5302	1·5108
·08770	2·576	2·544	2·513	2·481	2·450	2·418
	1·6045	1·5866	1·5672	1·5480	1·5298	1·5103
·1098	2·658	2·622	2·587	2·553	2·518	2·483
	1·6025	1·5848	1·5660	1·5464	1·5295	1·5090
·2020	2·989	2·942	2·893	2·843	2·792	2·744
	1·5931	1·5760	1·5576	1·5395	1·5215	1·5033
·4000	3·697	3·613	3·538	3·467	3·400	3·337
	1·5731	1·5564	1·5397	1·5224	1·5060	1·4892
·6000	4·400	4·288	4·182	4·090	4·003	3·917
	1·5521	1·5366	1·5211	1·5053	1·4898	1·4743
·8000	5·030	4·900	4·782	4·677	4·580	4·483
	1·5315	1·5166	1·5022	1·4875	1·4730	1·4586
1	5·642	5·490	5·349	5·212	5·090	4·975
	1·5122	1·4988	1·4850	1·4715	1·4578	1·4446

TABLE III.

Polarisations of chlorobenzene-carbontetrachloride solutions at different temperatures, the upper value being the polarisation (P) of the solution and the lower one the polarisation (P_2) of the solute.

Molar fraction of C_6H_5 Cl	Temperatures.					
	10°C	20°C	30°C	40°C	50°C	60°C
$C_2=0$	28·210	28·241	28·291	28·348	28·384	28·427
M=153·84						
$C_2=$ ·009201	28·742	28·756	28·789	288·27	28·853	28·884
M=153·46	86·04	84·22	82·42	80·42	79·36	78·10
$C_2=$ ·02113	29·424	29·419	29·435	29·456	29·450	29·465
M=152·97	85·66	83·99	82·43	80·78	78·83	77·55
$C_2=$ ·03690	30·301	30·278	30·265	30·247	30·223	30·233
M=152·32	84·88	83·47	81·78	79·81	78·22	77·38
$C_2=$ ·04258	30·610	30·592	30·565	30·541	30·510	30·490
M=152·08	84·57	83·45	81·70	79·85	78·31	67·88
$C_2=$ ·05796	31·464	31·397	31·348	31·291	31·238	31·231
M=151·44	84·35	82·69	81·03	79·12	77·62	76·81
$C_2=$ ·07562	32·401	32·331	32·225	32·148	32·097	32·041
M=150·72	83·63	82·33	80·31	78·60	77·48	76·22
$C_2=$ ·08465	32·888	32·784	32·671	32·581	32·500	32·460
M=150·34	83·47	81·91	80·03	78·35	77·01	76·07
$C_2=$ ·1055	33·924	33·796	33·697	33·592	33·512	33·408
M=149·48	82·38	80·90	79·53	78·05	76·99	75·64
$C_2=$ ·2140	39·046	38·822	38·690	38·440	38·238	38·047
M=145·00	78·85	77·69	76·60	75·51	74·43	73·38
$C_2=$ ·4810	49·08	48·77	48·45	48·22	47·97	47·79
M=133·97	71·60	70·91	70·21	69·65	69·10	68·68
$C_2=$ ·7427	56·57	56·28	55·99	55·68	55·42	55·15
M=123·16	66·39	65·99	65·59	65·14	64·78	64·41
$C_2=1$	62·76	62·47	62·18	61·88	61·65	61·45
M=112·53						

TABLE IV.

Polarisations of bromobenzene carbontetrachloride solutions at different temperatures, the upper value polarisation (P) of the solution and the lower one the polarisation (P_2) of the solute.

Molar fraction of C_6H_5Br	Temperatures					
	10°C	20°C	30°C	40°C	50°C	60°C
$C_2=0$	28·210	28·241	28·291	28·348	28·384	28·427
$M=153{\cdot}84$						
$C_2={\cdot}010014$	28·807	28·820	28·853	28·901	28·917	28·947
$M=153{\cdot}87$	87·83	86·06	84·41	83·57	81·60	80·35
$C_2={\cdot}02049$	29·417	29·414	29·436	29·448	29·459	29·477
$M=153{\cdot}90$	87·09	85·49	84·17	82·03	80·84	79·67
$C_2={\cdot}04110$	30·577	30·562	30·556	30·557	30·534	30·518
$M=153{\cdot}97$	85·80	84·71	83·40	82·10	80·69	79·31
$C_2={\cdot}04893$	31·010	30·980	30·969	30·949	30·922	30·914
$M=153{\cdot}99$	85·44	84·22	83·02	81·50	80·27	79·26
$C_2={\cdot}06420$	31·842	31·797	31·777	31·744	31·684	31·658
$M=154{\cdot}04$	84·78	83·63	82·59	81·24	79·78	78·76
$C_2={\cdot}07837$	32·618	32·550	32·523	32·432	32·381	32·340
$M=154{\cdot}08$	84·46	83·22	82·29	80·84	79·38	78·36
$C_2={\cdot}08770$	33·082	33·006	32·968	32·921	32·826	32·754
$M=154{\cdot}12$	83·76	82·57	81·62	80·33	79·03	77·74
$C_2={\cdot}1098$	34·246	34·142	34·064	34·006	33·868	33·801
$M=154{\cdot}18$	83·18	81·98	80·87	79·88	78·32	77·38
$C_2={\cdot}2020$	38·658	38·516	38·370	38·198	37·967	37·780
$M=154{\cdot}48$	79·93	79·10	78·19	77·11	75·82	74·73
$C_2={\cdot}4000$	46·69	46·30	46·17	45·97	45·77	45·60
$M=155{\cdot}10$	74·41	73·61	72·98	72·40	71·85	71·36
$C_2={\cdot}6000$	53·30	52·99	52·70	52·50	52·29	52·07
$M=155{\cdot}73$	70·03	69·50	68·97	68·60	68·23	67·84
$C_2={\cdot}8000$	58·52	58·27	58·07	57·88	57·76	57·60
$M=156{\cdot}36$	66·10	65·78	65·51	65·26	65·10	64·89
$C_2=1$	63·07	62·79	62·57	62·31	62·12	61·92
$M=156{\cdot}99$						

TABLE V.

Substance	Pα	A	A calculated from optical data	B	λ
C_6H_5 Cl	...86·4 at 10·C	31·2	30·3	15600	$1\cdot59 \times 10^{-18}$
	84·5 ,, 20·				
	82·8 ,, 30·				
	81·0 ,, 40·				
	79·5 ,, 50·				
	78·0 ,, 60·				
C_6H_5 Br	88·0 at 10·C	36·8	33·4	14500	$1\cdot53 \times 10^{18}$
	86·2 ,, 20·				
	84·7 ,, 30·				
	83·1 ,, 40·				
	81·7 ,, 50·				
	80·4 ,, 60·				

A Method of Measuring the Resistance of Electrolytes at Low Frequencies

Comparison of electrolytic resistance at low and radio frequencies.

By

J. A. C. Teegan, M.Sc., A.Inst.P.

1. *Introduction.*

The resistance of electrolytes at high frequency was first investigated by Professor J. J. Thomson in 1899. [1] Using a hertz oscillating circuit he observed no change in the ohmic resistance of electrolytes up to frequencies of the order 10^8. Subsequently a very accurate method of measuring electrolytic resistance at high frequency was devised by J. J. Dowling and Miss Preston. [2] They employed a H.F. oscillation valve circuit, the principles involved being an extension of the ultra-micrometer methods described by Dowling before the British Association in 1921. [3] At a frequency of $\cdot 5 \times 10^6$ (approx.) they detected no change in the ohmic resistance offered by a solution of copper sulphate to high and low frequency currents. The problem, however, seemed worthy of further investigation, and in this paper some experiments, on similar lines, over a wide range of frequencies are described.

In the experiments referred to above the electrolytic resistances at low frequency were measured by the Kohlrausch bridge method. In this paper a new method of measuring resistance (metallic and electrolytic), at low (audible frequency), is described. The principles involved are similar to those employed by Dowling, except for a modification in the type of oscillation circuit employed. It has been found very satisfactory for this work, and is, on account of its high sensitivity, especially suited for the determination of small resistance changes.

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[1] J. J. Thomson, Proc. Roy Soc., Vol. XIV, 1889.

[2] Dowling and Preston, Phil. Mag., 1922.

[3] British Assoc. Edinburgh in 1921, and Royal Dub. Society, 1920.

2. *Experimental Arrangements.*

Many trials of possible oscillation circuits, suitable for low frequency work, were carried out, the following being found the most satisfactory. It consists of a Hartley circuit (fig. 1).

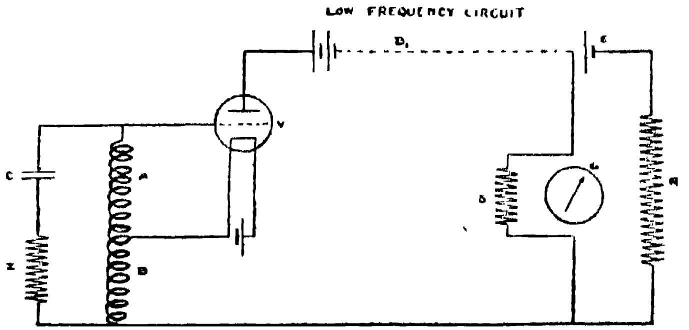

Fig. 1.

A and B are two coils of many turns wound on a cylindrical former of 4 inches diameter containing a soft iron core. C is a variable condenser of range (·01 to ·1UF) V an ordinary R valve taking ·5 amp. in filament. H. T. a battery of 30 volts.

To use a sensitive galvanometer a zero shunt arrangement ER is employed. It consists of a 2-volt cell E joined in series with a resistance R, the whole being in parallel with a shunted galvanometer GS. If C is any value of the anode circuit, a current $\frac{R}{R+G}(C-C_0)$ passes through the galvanometer where, $C^\circ=\frac{E}{R}$, and for values of C approximating to C_0 a sensitive galvanometer can be used to measure variations in

C. The galvanometer employed was of the Gambrell moving coil type (sensitivity 300 scale-divisions for microamp). The frequency of the circuit is about 1,500.

The anode current for different values of the capacity C was measured, and anode current-capacity curves obtained, first with no resistance, and then with resistances 50,100,200, etc., ohms at Z, in series with the condenser C. The introduction of resistance reduces the anode current, and corresponding to a capacity ·05 μF. the anode current decreases linearly with the resistance up to 200 ohms. Setting the condenser at this value, R was then adjusted until the galvanometer was at Zero, with no resistance at Z. Resistance in steps of 10 up to 100 ohms were then introduced, and a linear relation between galvanometer deflection and resistance obtained (fig. 2).

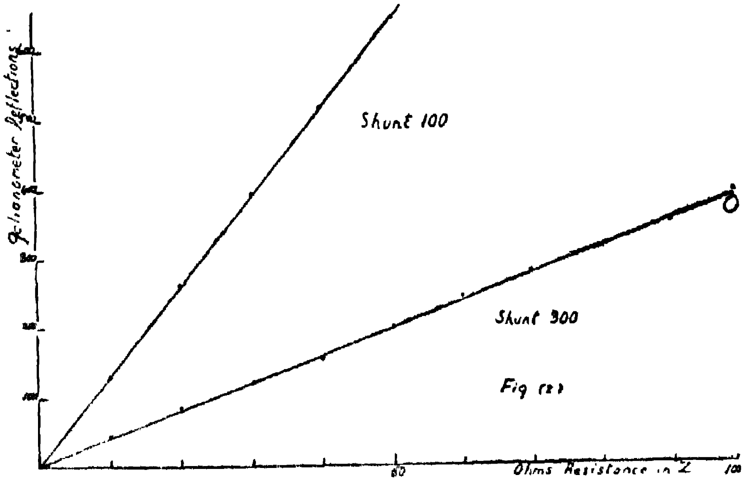

Fig. 2.

A similar linear relation was obtained when a variable electrolytic resistance of copper sulphate was introduced at Z.

The direct proportionality between galvanometer deflection and resistance (electrolytic or metallic) affords a method of measuring electrolytic resistance by comparing it with wire resistances of known value. The electrolytic resistance E is placed at Z, R is varied until the galvanometer is at zero. One wire of resistance $r_1 < E$ is then placed at Z, and the galvanometer deflection g_1, determined. Similarly the deflection g_2 corresponding to the second resistance $r_2 > E$ is obtained. Assuming, then, that the three resistances are within the range of the straight portion of the curve,

$$E = r_1 + \frac{g_1(r_2 - r_1)}{g_2 - g_1}$$

In one set of observations on three different copper sulphate solutions the following results were obtained:—

TABLE I.

1 Resistance	Galvanometer	2 Resistance	Galvanometer	3 Resistance	Galvanometer
r_2(=40 ohms)	53	r_2(=60 ohms)	25	r_2(=80 ohms)	31
E	0	E	0	E	0
r_1(=20 ohms)	−38	r_1(=40 ohms)	−64	r_1(=60 ohms)	−57
(1) E=28·35	(11)	E=53·25 ohms	(111)	E=72·96 ohms	

These resistances measured by Kohlrausch bridge method had values equal to 28·1 ohms, 53·2 ohms and 73·1 ohms, which are in good agreement with those obtained by the new method.

A consideration of fig. 2 shows that with the galvanometer shunt 100, 1 division correspond to $\frac{1}{13}$ ohms. If the galvanometer were unshunted this would correspond to a sensitivity of $7{\cdot}6 \times 10^{-4}$ ohm per div.

Thus extremely small variations should be measurable. Actually however it is exceedingly difficult to work with the galvanometer unshunted, owing to a creeping caused by fluctuation, in the batteries. Cells in very good condition are absolutely essential, when employing the method for high sensitivity work. It is advisable to use zero-shunt cells of construction similar to those used in the high tension battery. Employing a high tension battery composed of a number of small accumulator-cells it has been found quite easy to work with the galvanometer shunt $\frac{1}{3}$.

For the comparison of electrolytic resistances at low and radio frequencies the circuit employed by Dowling was used for the high frequency determination, that described above being employed for the low frequency measurement. To carry out the measurements simultaneously, these two circuits were incorporated in one, in the manner indicated in the fig. 3.

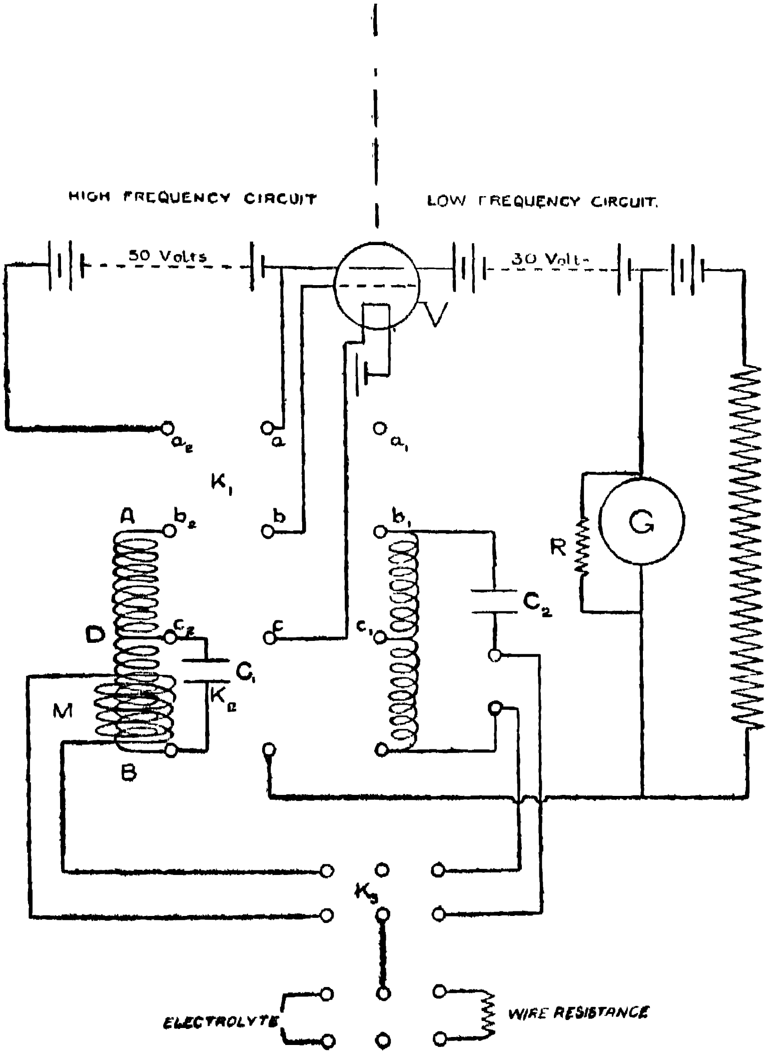

Fig. 3.

Two six way keys K_1 and K_2 are arranged as shown. The plate, grid, and filament of the value are attached to points a, b, c. When these are connected to $a_1b_1c_1$ the low frequency circuit is in action, when connected to $a_2b_2c_2$ the high frequency circuit is in action. Two additional keys K_3 and K_4 enable the current to be alternately connected to the wire or electrolytic resistance.

The coil AB in the H.F. circuit was identical with that used by Dowling, consisting of 200 turns of No. 22 copper wound on a frame 10 cms. square. The resistance was connected in series with a second coil M placed co-axial with AB so that the oscillation in BDC induced oscillations of the same frequency in M and the resistance. (Alteration of the position of D gave a range of frequencies.) In high frequency determination of this type the following sources of error are of importance :—

1. Induction effect in wire resistance.
2. Skin effect in wire resistances or electrolyte.
3. Capacity and induction effects due to a lack of symmetry in wire leads, etc.
4. Polarisation electrode capacity effects.

The use of specially designed non inductive resistances, made by Tinsley & Co., eliminated errors due to induction. For the change in resistance of a wire due to skin effect, Fleming gives the formula,

$R=38{\cdot}4\ N^2\ drnp$ ($N=$ no of turns, $d=$ diam. of wire, $n=$ frequency $p=$ sp. resistance). Substitution in this formula for wires used in these experiments gave a maximum value of $DR=1$ per cent.

All effects due to possible stray induction or capacity effects were reduced to a minimum, by arranging the apparatus (leads, etc.) as symmetrically as possible.

The effect of polarisation upon the apparent resistance of an electrolyte is expressed by

$$R^1=R\left(1+\frac{1}{2}\ \frac{P^2}{p^2R^2}\right),\quad \text{where } p=2\pi n \text{ and } P=\frac{2}{cA}$$

A being area of the electrodes and C the "Electrode capacity" per unit area. For the electrodes used in these experiments the factor P in the correction term is small, p is always great, the minimum value of n being $\cdot 2 \times 10^6$.

3. *Experimental Results.*

The electrolytic cell employed consisted of a cylindrical glass tube 1·25 cms. diam. fitted with cylindrical electrodes (gold plated). The length of the electrolytic column was variable. Solutions of copper sulphate and sodium chloride varying in strength from $\frac{N}{10}$ to N were measured over a range of frequencies extending from $\cdot 2 \times 10^6$ to 10^6. The method of making measurements at high frequency was identical to that employed at the low frequency, the electrolyte being compared with the same two wire resistances. The results shewn in Table II for the values of the resistance of a solution of copper sulphate (low frequency resistance=93·42 ohms), measured over a range of high frequencies shows that to within ·5 per cent. the resistance of the electrolyte is unaltered at high frequencies.

TABLE II.

Frequencies	Resistance (ohms)
$\cdot 23 \times 10^6$	93·40
141×10^6	93·47
$\cdot 42 \times 10^6$	93·44
$\cdot 46 \times 10^6$	93·5
$\cdot 48 \times 10^6$	93·43
$\cdot 5 \times 10^6$	93·40
$\cdot 61 \times 10^6$	93·05
$\cdot 90 \times 10^6$	93·52
10^6	93·00

Similar experiments carried out on copper sulphate of various strengths and on sodium chloride (N) indicated the same agreement between electrolytic resistance at high and low frequency. In making these measurements it was found necessary to have the electrode chemically clean and perfectly polished, as in experiments in which the electrodes had been in contact with the solution for some time quite large apparent resistance changes were observed. The high frequencies were measured by a special resonance-wave meter circuit. [1]

On carrying out experiments in which copper electrodes were used instead of gold this agreement between the resistance at high and low frequency no longer held good. In the case of copper electrodes in copper sulphate solution very large variations in apparent resistance at high frequencies were observed, which seemed to exhibit a certain regularity with increase of frequency. In one series of experiments over a range of frequencies from $\cdot 4 \times 10^6$ to 10^6 the copper sulphate solution commenced to exhibit a gradual increase up to 10 per cent. for a frequency of 10^6. (It is of interest that at the frequency of $\cdot 48 \times 10^6$ employed by Dowling and Preston this change could not have been noticed.)

Experiments were then devised to investigate the apparent resistance change under different conditions of current density, by employing a Moullin voltmeter to measure the potential drop across a column of the electrolyte, the current being recorded by a thermo vacuo element. Indication of the apparent resistance change was again observed in case of the copper electrodes, whilst no change was observed when gold electrodes were employed. Unfortunately these experiments have been interrupted by the departure of the author from Europe, but it is hoped to continue this line of investigation at an early date. Possibly the effect is in the nature of an obscure polarisation capacity effect or the result of chemical action. A considerable amount of data is, however, required before any attempt can be made to account for it.

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[1] Dowling and Mc. Henry, Engineering, 1921.

4. *Summary.*

A method of measuring metallic and electrolytic resistances at low frequency capable of great precision is described. A series of experiments on resistance of electrolytes at high and low frequencies indicate that they undergo no change at frequencies at 10°. Apparent resistance changes have been obtained when copper electrodes are substituted for gold electrodes. These are probably in the nature of polarisation or chemical effects.

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31

Studies in X-Ray Diffraction—Part I

The Structure of Amorphous Carbon

By

P. KRISHNAMURTI

(*Plate XIV*)

(*Received for publication, 15th November, 1929*)

1. *Introduction.*

The question whether amorphous carbon represents a third modification of carbon or whether it is only finely-divided graphite was first examined by Debye and Scherrer[1] by their powder method. Several varieties of amorphous carbon such as sugar charcoal, carbon from burnt acetylene naphthalene and petroleum, retort carbon, anthracite, gave similar X-ray patterns, where the prominent lines of graphite were present in the same position, though considerably broadened out. The next investigator in this field was G. Asahara[4] who examined 35 different specimens of graphite and amorphous carbon, using the tungsten radiation, and came to the same conclusion, *viz.*, that amorphous carbon was nothing but very finely-divided graphite. No attempt was made in either case to observe the phenomena at small angles to the primary beam, or to find out the exactness of the coincidence between the graphite and amorphous carbon patterns by microphotometering them or otherwise. The considerable divergence in the physical and chemical properties of graphite and amorphous carbon, *viz.*, specific gravity, electrical conductivity, diamagnetic susceptibility, adsorptive activity, oxidation products, etc., still induced many workers to consider amorphous carbon as quite distinct from graphite. Among the physical properties, the diamagnetic susceptibility shows a marked difference. The susceptibility of amorphous carbon agrees very closely with that of diamond and is only about one-tenth that of graphite.[20] Among chemical properties, the oxidation products are different in the two cases, graphite giving rise to graphitic acid while amorphous carbon yields only mellitic acid or benzene-hexacarboxylic acid on vigorous oxidation. Again, amorphous carbon can be prepared in a very active form, while graphite has very little adsorptive activity.

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[1] References are to the bibliography cited at the end of the paper.

2. *Previous Investigations on Carbon.*

It will be realised that since amorphous carbon is prepared under different conditions from different substances mostly hydrocarbons, they show variations among themselves in several physical and chemical properties. The two following considerations are very important regarding a sample of amorphous carbon. (1) *Purity.* Since the samples are prepared by incomplete combustion of hydrocarbons or by pyrogenetic decomposition of compounds containing a high percentage of carbon in addition to hydrogen and oxygen, the carbons are always associated with varying amounts of oxygen and hydrogen. (2) *Temperature of formation.* This factor is the most important and decides nearly all the various physical and chemical properties of the carbon. In fact Hofmann and Rochling[9] have prepared a variety of " Hochglanz " carbon when it seperates out from hydrocarbons on smooth porcelain heated to 750-800°C. This possesses considerable lustre and hardness, but the X-ray diagram gives broad bands whose positions are said to agree with those of graphite. Recently, Else Koch-Holm[10] has examined this question thoroughly by preparing a number of carbons at different temperatures up to about 2000°C. He finds them all to show the prominent graphite lines, but the line-breadths vary in the different cases, and the lines get sharper, the higher the temperature at which the carbon is prepared. For instance, the carbon prepared at 2000°C has dimensions of about 105A [calculated from the (002) reflection] and 304A [from the (111) reflection] while sugar charcoal shows only 45A (from the 111 reflection). He also finds that in the Hochglanz carbon the extent of each particle at right angles to the 001 plane is only about a third of its value in the plane, so that the particles are quite anisotropic. His observations on the sizes of the crystallites in Hochglanz carbon are in agreement with those of Hofmann and others.[14]

Another group of investigators[12] Ruff, Schmidt, Olbricht are inclined to the view that amorphous carbon is a "para crystalline" state of matter bridging the amorphous and crystalline states more effectually than what is known as the "mesomorphic" or liquid crystal state. Clark and Alm[15] from X-ray and chemical considerations are in agreement with this view. They found that by subjecting the amorphous carbon to heat treatment, *e.g.*, at 1100°C, its adsorption activity diminishes, the solubility in oxidation media decreases and so also does the specific resistance, which comes down to values obtained with graphite. On the other hand they find that the X-ray diagram remains essentially unchanged. As the heating is increased, they find the amorphous ring to get sharper, and gradually the graphite lines at smaller and then at larger angles make their appearance.

Finally reference should be made to the work of Lowry and Bozorth,[17] who have investigated the adsorption activity and X-ray diagrams of carbon obtained by exploding graphitic acid prepared by oxidising graphite to different extents. They find that the most finely-divided variety shows as much as one-fourth the adsorptive activity of charcoal. The X-ray reflection method using the K_α radiation of Mo and the compressed material gave three diffuse bands. The (002) spacing was found to be 3·6A while the coarse variety gave only 3·4A. This observation is very important, since all the workers seem to find the graphite and amorphous carbon spacings identical within limits of experimental error.

3. *Results.*

It was at this stage that this problem was taken up by the present author for thorough investigation by the X-ray method. Special attention was paid to the scattering at small angles to the primary beam, and the positions of the maxima were obtained accurately by microphotometering the patterns. The K radiation of copper and the pinhole method were used as usual. The results with about a dozen samples of amorphous carbon showed two remarkable features not observed before. Firstly, *a strong scattering* at small angles was observed in every case, the intensity of which was comparable to and sometimes greater than that of the first ring. Secondly, the position of the first maximum did not coincide with that of graphite. The spacing of the (002) reflection in graphite was 3·41 A, while in amorphous carbon an average value of 3·8 A was obtained. It was more with some very finely-divided varieties, and slightly less in a few cases. The outer maximum however, was very diffuse, and its position varied within very small limits. A description of each kind of carbon examined, together with the characteristic features of its X-ray pattern will be given below.

(1) *Benzene and naphthalene carbons* :—These were obtained by burning benzene and naphthalene and allowing the soot to deposit on smooth porcelain. The samples were afterwards heated in a small evacuated glass bulb over the Bunsen flame for about 15 minutes, cooled and pressed into the cell so that the thickness of the sample was 1 mm. in every case.

The X-ray patterns were similar for both, and consisted of (1) the strong scattering at small angles extending to about 13·3 A, (2) A broad ring (spacing 3·73 A), (3) A faint but distinct outer ring (spacing 2·14 A). The region between the inner scattering (corona) and the first ring was fairly clear.

(2) *Sugar charcoal:*—Merck's canesugar was charred in a crucible, and heated with lid on over a Bunsen flame for $\frac{1}{2}$ hour and afterwards heated at the blast lamp for the same period. It was then powdered in an agate mortar and introduced into the cell between thin mica windows.

The X-ray diagram showed (i) An intense corona at small angles, (ii) A diffuse ring at 3·83 A, (iii) A very diffuse outer ring at 2·12 A. There was a good deal of scattering between the corona and the first ring. The outer ring was more diffuse than with benzene carbon.

The above charcoal was treated with conc. nitric acid at first in the cold, and afterwards with slight warming. Three treatments were given, the product being washed throughly after each treatment. It was finally washed free of acid and ignited at the blast lamp for $\frac{1}{2}$ hour. The X-ray pattern of the treated sample showed a remarkable change, the corona becoming considerably more intense than in the previous case. The first ring was more difuse and fainter, but the positions of the maxima were unaltered.

Kahlbaum's sugar-charcoal was examined as such. The pattern differed from those of the two samples described above. The corona was less intense but extended over a larger area, and its separation from the first ring was just perceptible. The outer ring was extremely faint and diffuse, more than in the previous cases. It was also found that a sample of sugar-charcoal prepared by charring at a low temperature (the Bunsen flame) had the same characteristics in its X-ray pattern.

(3) *Active charcoal (Kahlbaum):*—The pattern was characterised by the large intensity of the corona and its

abrupt ending. The position of the first maximum agreed more with that of the benzene charcoal. The outer ring however was so diffuse that accurate measurement of the spacing was not possible.

(4) *Carbon from C_2Cl_6*:—Freshly-cut sodium was introduced into a pyrex test-tube, melted and carbon hexachloride was introduced in small amounts at a time. Each addition was followed by a flash, and carbon deposited at the bottom and sides of the tube. The product was then treated with absolute alcohol to dissolve the sodium, and finally boiled up with distilled water several times and washed thoroughly till free from all soluble impurities. It was then dried in an air oven at about 120°C and ground in an agate mortar till it was obtained in a compact, dense form, after which it was pressed into the cell. No mica was used in this case.

The X-ray pattern showed a slightly smaller extent of the corona. The two maxima were however very broad, and their positions were very near those of sugar-charcoal. The rings were the broadest of all the above patterns.

(5) *Carbon from CCl_4*:—This was prepared in the same way as above. Addition of each drop of CCl_4 to the sodium was followed by a tiny explosion and carbon separated out according to the equation:

$$CCl_4 + 4Na \longrightarrow 4NaCl + C.$$

The carbon was collected, washed thoroughly, ground in the agate mortar to a compact mass and pressed into the cell.

The X-ray pattern showed a strong corona just as in C_2Cl_6 carbon. But the first ring was even broader and fainter, and the spacing had increased to about 4·0A. The second ring was not visible, and only a general darkening in that region could be noticed.

(6) *Acheson Graphite*:—Hilger's specimen for spectroscopic use was converted into a fine powder and enclosed between thin mica plates. The pattern showed all the graphite rings, of which the (002) and (111) reflections were strong.

The fine powder was shaken up with 1 % tannic acid solution for 3 days, allowed to stand for two days and the suspended graphite collected by centrifuging and dried. In its pattern the positions of the lines were the same as before, but a strong intensity of scattering in the neighbourhood of 0^0 and a general scattering ending with the first ring were prominent. A similar effect observed with natural graphite has already been reported.[18]

Several other varieties of amorphous carbon, *viz.*, cocoanut charcoal, gelatine charcoal, wood charcoal, filterpaper charcoal, etc., were examined, but the patterns showed essentially the same features as those described above. The strong small-angle scattering and the two broad maxima were observed in all cases. The following table contains the results obtained with the samples of carbon above described. The measurements were made visually and agreed with those of the microphotometer curves. The spacings were calculated as usual from the Bragg formula,

$$a = \frac{\lambda}{2 \text{ Sin } \frac{\theta}{2}}.$$

TABLE I.

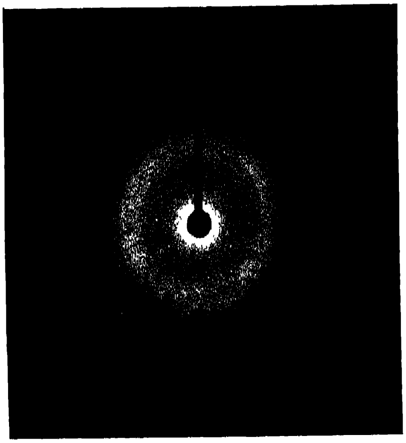
Sample.	Extent of corona.		Inner Ring.		Outer Ring.	
	θ	Spacing in A.	θ	Spacing in A.	θ	Spacing in A.
1 Benzene carbon.	6°38′	13·3	23°48′	3·73	42°15′	2·14
2. Sugar charcoal.	6°38′	13·3	23°12′	3·83	42°34′	2·12
3. Active charcoal	6°38′	13·3	23°42′	3·75	42°15′	2·14
4. C_2Cl_6 carbon.	5°50′	15·1	23°24′	3·80	42°34′	2·12
5. CCl_4 carbon.	5°36′	15·8	22°12′	4·00	—	—
6. Acheson graphite.	—	—	26°6′	3·41	43°48′	2·06

4. *Discussion of Results.*

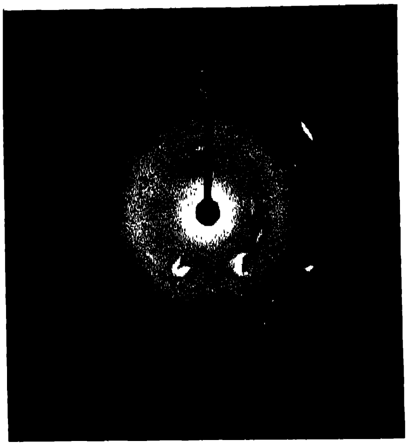
Small angle scattering :—It will be seen that one feature characteristic of all the patterns is the presence of the strong scattering at small angles to the primary beam. Acheson graphite does not show this scattering, though there is some evidence that when prepared in the colloidal form, it scatters also in the neighbourhood of 0°. The extent of the small angles scattering in the different varieties of amorphous carbon (measured up to the point where the intensity shows a rapid decrease) averages 13·3A, though there is still considerable scattering extending right up to the first ring, after which there is a sudden diminution of intensity. The patterns however show differences in the intensity distribution of the small angle scattering. In treated sugar charcoal and in Kahlbaum's active charcoal, this scattering far exceeds the intensity of the first ring, the benzene, C_2Cl_6 and CCl_4 carbons following in that order. Kahlbaum's sugar-charcoal shows an even distribution of scattering extending over a larger area.

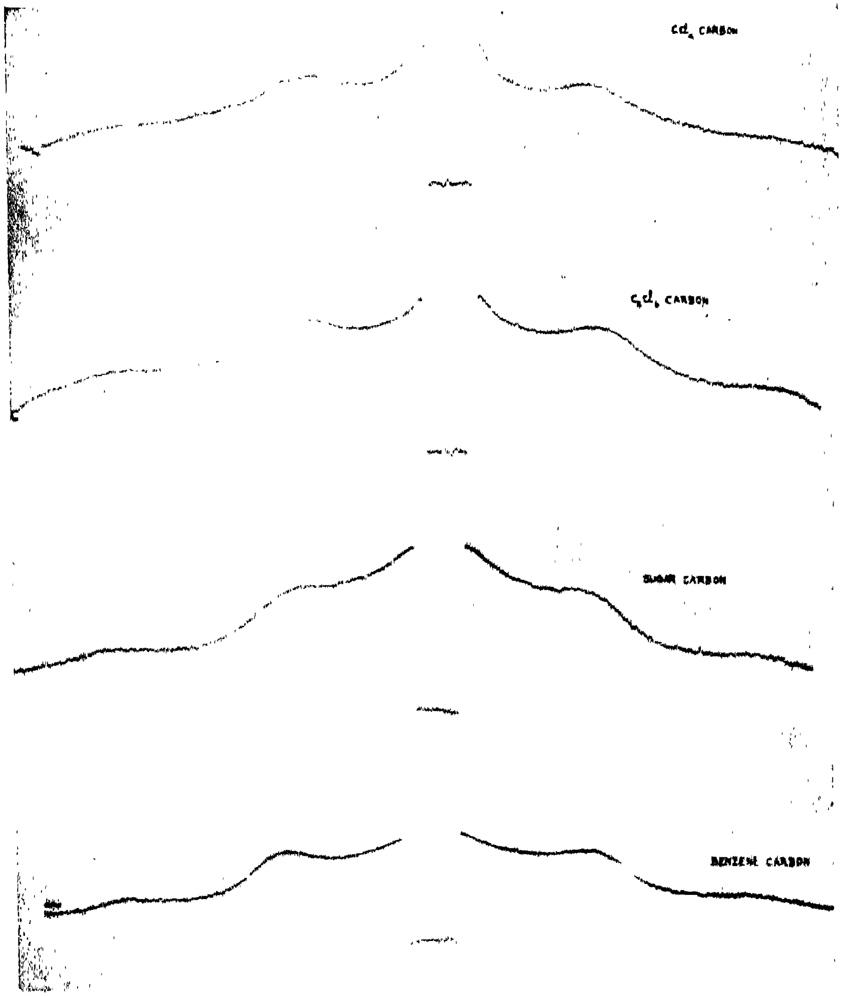
The significance of these observations will be more evident when we consider the origin of this small angle scattering. A scattering of this type has been observed previously by the author in the patterns of dilute solutions of canesugar and other substances, and ascribed to the scattering by randomly distributed sugar molecules. This agreed with the further observation that the extent of the corona varied with the size of the dissolved molecule. Extending this idea to the diffraction by colloidal substances like dextrin and gelatin, the author obtained probable values for the sizes of the dissolved molecules from the extent of the small angle scattering by the application of Bragg's law. But the values were only quite approximate since in calculating the molecular weight, the particles or molecules were regarded as cubical, which is of course only an ideal case.

C_2Cl_6 Carbon



Active Charcoal





Microphotometer curves

X—Ray Diffraction by Amorphous Carbon.

Considerations of light-scattering phenomena in liquids * help us to a great extent in further understanding this question. It has been pointed out by Raman and Ramanathan[8] that at small angles of scattering, X-ray phenomena are analogous to those of light-scattering. In the optical case we are well aware that a large increase in light-scattering is observed in two simple cases, (1) when the anisotropy of the molecule is very pronounced, the intensity of the scattered light is increased in the ratio $\frac{6(1+r)}{6-7r}$ where r is the percentage of the imperfectness of polarisation, (2) in cases of "critical opalescence" where the scattering mainly arises from innumerable irregular surfaces bounding the clusters of molecules. Hence, in the X-ray region, we might expect a large scattering at small angles in the case of anisotropic particles with irregular surfaces surrounding clusters of molecules. We can therefore postulate the existence of finely divided particles of carbon essentially anisotropic and oriented at random, the arrangement of the carbon atoms in the particles also not characterised by that uniformity of arrangement present in the crystal.

Position and breadth of the lines :—From table I it will be evident that the spacing of the first ring in every sample of amorphous carbon is larger than that of the corresponding graphite ring. This fact is very important and seems to have escaped the observation of previous workers. The result of Lowry and Bozorth[17] that the spacing of the first ring in the finely-divided graphite prepared by exploding graphitic acid is 3·6A while the same spacing in the coarser variety is 3·4A, is very interesting in this connection. There can be no doubt that the amorphous carbons examined here possess even smaller particle size, and hence the larger value for the spacing, *viz.*, 3·8 4A is certainly to be expected. The graphite lattice, therefore, if present is considerably distorted. The carbon prepared from CCl_4 shows this effect markedly, the spacing being as high as 4A. The outer ring which is faint as well as diffuse in all these cases has a spacing which is only slightly larger than that in graphite.

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* See numerous papers by Prof. C. V. Raman and his pupils in the Indian Journal of Physics.

The lines in the patterns are so broad and diffuse that measurement up to the half-intensity limit is not possible. But a comparison of the patterns shows that the line-breadth increases in the following order: benzene carbon, sugar charcoal, active charcoal, C_2Cl_6 carbon and CCl_4 carbon. In the last case, the second maximum is barely visible. Tammann[3] has pointed out that CCl_4 carbon is the most finely-divided, but he was unable to detect a maximum in the X-ray pattern of the sample, but only a general scattering. This was probably because the amount of carbon used was insufficient to give a pronounced maximum.

The structure of the particles :—From the characteristics of the X-ray diagrams we have now to work out the probable shape and size of the particles present in the different samples of amorphous carbon. In the case of liquid hexamethylbenzene, the present author has shown that the first ring with a spacing of 8·2 A represents periodicities in the plane of the benzene ring, while the spacing of the outer ring (4·2 A) represents the thickness of the molecule.* In a similar way taking the spacing of the first ring as a measure of the thickness of the particle, and the spacing corresponding to the small angle scattering as the average dimension in the plane of the ring (001 plane), the total volume of the particle is :—

$$(13{\cdot}3)^2 \times 3{\cdot}83 = 677{\cdot}6\,A^3$$

in the case of sugar charcoal, Taking the density of sugar charcoal as 1·75 we get for the number of carbon atoms in any particle :—

$$\frac{677{\cdot}6 \times 1{\cdot}75}{12 \times 1{\cdot}66} = 59{\cdot}5 \text{ (nearly 60)}$$

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* Krishnamurti, Ind. J. Phys., 4, 449 (1930).

Hence an average particle could be pictured as a unit with $(13{\cdot}3)^2$A as cross-section and 3·83A as the thickness, containing about 60 atoms of carbon. This brings out the anisotropy of the particle, the dimension in one direction being more than thrice the value perpendicular to it. There is the possibility of there being particles bigger in size than the one indicated which may be present to a limited extent.

The above picture of the carbon complex which is essentially two-dimensional receives support from chemical and other considerations. The oxidation of amorphous carbon yields mellitic acid or benzene hexacarboxylic acid but not graphitic acid. The latter of course yields mellitic acid on further oxidation. We know from the work of Mrs. Lonsdale that in hexamethylbenzene all the carbon atoms lie in the same plane. Since mellitic acid is obtained from hexamethylbenzene by oxidation, it is resonable to suppose that the carbon atoms are similarly situated in the mellitic acid molecule. Hence, a partial structure for the amorphous carbon particle is indicated in fig. 1 with a minimum of 24 atoms of carbon most of them lying in the same plane, which on oxidation breaks up at the places indicated by dotted lines giving mellitic acid. A model of the particle of amorphous carbon having the dimensions arrived at from X-ray data is shown in fig. 2.

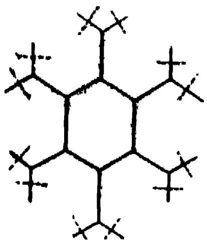

FIG I.

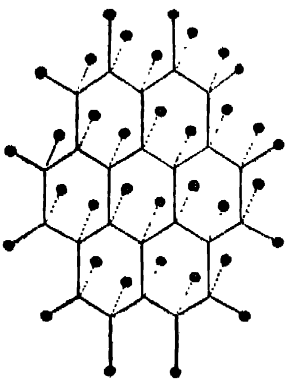

FIG. 2.

All the carbon atoms lie in two parallel planes and the dimensions in the plane will be just greater than the length of the anthracene molecule, so that the value of 13·3A as compared to the 11·6 A of anthracene is quite probable. The corner atoms may all be of carbon, or may be hydrogen or oxygen or nitrogen according to the conditions under which the carbon is prepared. All the carbon atoms are joined by a loose bond to similar carbon atoms in the next layer, and the two layers together constitute the carbon particle present in amorphous carbon. The end carbon atoms may not have counterparts in the next layer, so that the total number of carbon atoms will be $36+24=60$, the number arrived at previously from X-ray data. This model can also explain the adsorptive power of charcoal since the large number of end carbon atoms are held together by distorted and strained valency bonds which may break up under suitable conditions.

Amorphous nature of charcoal :—It is well-known that amorphous solids show X-ray patterns characteristic of liquids, in that they show the presence of one or more ill-defined bands. The purely "amorphous scattering" where no maxima are present could only exist in the case of ideal gases. The pattern for amorphous carbon is remarkable in that it shows both a scattering at small angles, usually absent in liquid patterns, as well as a few broad maxima. The varying nature of the small angle scattering with the method of preparation and treatment, and the increase in definition of the rings with an increase in the temperature of formation suggest that amorphous carbon represents an intermediate state through which the atoms of carbon have to pass before attaining the orderly arrangement underlying the graphite structure. G. L. Clark,[15] O. Ruff and others consider this as the 'para-crystalline' state, and this is quite justifiable inasmuch as it distinguishes it from an ordinary amorphous solid, and since there is always a tendency to pass over into the true crystalline state of graphite under favourable conditions.

5. *Summary and Conclusion.*

(1). An entirely new phenomenon appearing at small angles to the primary beam in the diffraction patterns of all the varieties of amorphous carbon, *viz.*, a strong scattering extending to about 7° has been observed. Sugar charcoal, benzene and naphthalene charcoals, carbon obtained by charring ash-free gelatin, and carbons prepared by reacting C_2Cl_6 and CCl_4 with molten sodium, all these showed the small angle scattering in a marked manner.

(2) The patterns showed two rings in addition to the central scattering, the first and prominent ring corresponding to the (002) reflection of graphite, having a spacing of about 3·8 A as compared to 3·4A of graphite. The outer ring was fainter and broader, and showed a spacing of 2·12 A comparable to the (111) spacing of graphite (2·06A). In CCl_4 carbon, the spacing of the first ring was 4·0A and the second ring was hardly visible, showing it to be the most finely-divided variety examined.

(3) The observations accord with the idea that in the amorphous state, the carbon atoms join together in clusters, forming highly anisotropic units essentially two-dimensional, the thickness being about one-third the length or breadth. Assuming that the central scattering is due to the dimensions in the plane of the particle and the first ring to its thickness, a rough calculation gives about 60 atoms of carbon per unit. This picture of the carbon particle agrees with chemical evidence, mainly its oxidation to mellitic acid and adsorptive properties. A diagram of the particle is given which shows the dimensions and number of carbon atoms in each particle of the right order of magnitude.

It can be pointed out here that a study of the small-angle scattering not only in the case of carbon, but also in the case of finely-divided bodies may give an indication of the size and distribution of the particles, especially when the latter approach molecular dimensions.

Note added to proof, dated 7th Sept., 1930:—The author was enabled to study the patterns given by colloidal graphite prepared by exploding graphitic acid in a vacuum, through the courtesy of Dr. H. H. Lowry who was kind enough to send him two samples. Fe Kα radiation was used, and both varieties (II and III)[17] gave a ring at 31° 3′ corresponding to 3.61A in excellent agreement with the results obtained by Lowry and Bozorth. In addition, a very intense scattering at small angles to the primary beam was observed in both cases, which was more intense and at smaller angles than with the other samples of amorphous carbon described in the above pages. This is probably because the particle size is greater in the colloidal graphite than in the other amorphous carbons.

In conclusion, the author desires to thank Sir C. V. Raman, F.R.S., for his keen interest in this work.

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Bibliography.

(1) Debye and Scherrer, Phys. Zeit. *17*, 277 (1916) ; *18*, 291 (1917).
Constitution of graphite and amorphous carbon:.

(2) Hull, Phys. Rev. *10*, 661 (1917).
A new method of X-ray crystal analysis.

(3) Tammann. Z. Anorg. Chem., *115*, 145 (1921).
Carbon formed by the action of mercury on CCl_4 etc.

(4) Asahara, Jap. Jour. Chem. *1*, 35 (1922).
On the nature of graphite and amorphous carbon.

(5) Wever, Mitt. a.d.K.W. Inst. fur Eisenforschung *4*, 81 (1922).
X-ray study of graphite and amorphous carbon.

(6) Poch, Anales. Soc. espanola Fis. Quim., *21*, 291 (1923).
X-ray investigations of charcoals.

(7) Piriani and Fehse, Z. f. Elektrochem, *29*, 168 (1923).
X-ray study of pure graphite.

(8) Raman and Ramanathan, Proc. Ind. Assn. Cult. Sci., *8*, 127 (1923).
The diffraction of X-rays by liquids, solutions and amorphous solids.

(9) Hofmann and Rochling, Ber. *56*, 2071 (1923).
Vitreous carbon ; a special form of crystalline carbon.

(10) Hassel and Mark, Z.f. Phys. *25*, 317, (1924).
Crystal structure of graphite.

(11) Bernal, Proc. Roy. Soc. A *106*, 749, (1924).
Crystal structure of graphite.

(12) Ruff, Olbricht and Schmidt, Z. Anorg. Chem. *148*, 313, (1925).
Amorphous carbon and graphite.

(13) Ebert, Dissertation, Greifswald, 1925.
The structure of graphite.

(14) Hofmann and Hofmann, Ber. *59*, 2433 (1926).
Gas carbon as the first of a series of black carbon crystals.

(15) Clark, Coll. Sym. Monograph, *4*, 155 (1926).
X-rays and colloids.

(16) Else Koch-Holm, Wiss. Veroff. Siemens-Konzern, *6*, 188 (1927-28).
Investigations on the structure of crystalline carbons.

(17) Lowry and Bozorth, J. Phys. Chem., *32*, 1524 (1928).
The adsorption of gases by graphitic carbon II. X-ray study.

(18) Raman and Krishnamurti, Nature, *124*, 53 (1929).
A new X-ray effect.

(19) Mahadevan, Ind. J. Phys., *4*, 79 (1929).
X-ray study of coal.

(20) Paramasivan, Ind. J. Phys., *4*, 139 (1929).
The anomalous diamagnetism of graphite.

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Studies in X-Ray Diffraction : Part II

Some Colloidal Solutions and Liquid Mixtures

By

P. Krishnamurti.

(Plate XV.)

(Received for publication, 15th November, 1929.)

1. *Introduction.*

The previous work of the author on molecular and colloidal solutions and on liquid mixtures using the X-ray method has led to some important results. For instance, in a dilute solution of cane sugar, the random arrangement of the sugar molecules produced a strong scattering at small angles to the primary beam.[7] The extent of the scattering was shown to depend on the size of the dissolved molecule, and hence the small angle scattering in some colloidal solutions of dextrin, gelatin and sodium oleate was studied,[8] and probable values for the molecular weights of these substances were obtained. While dextrin and gelatin were molecularly dispersed in their solutions, sodium oleate solutions consisted of micelles, each micelle being composed of a number of simple molecules joined together. This conclusion was based on the evidence that the X-ray diffraction pattern even of a dilute solution of soap showed the ring due to the latter in addition to the water ring. This was further supported by the independent evidence of McBain obtained from other measurements. In the present investigation some more of the colloidal substances were examined, *viz.*, soluble starch, tannic acid and gum arabic both in the solid state and in solutions of different concentrations. A few liquid mixtures were also examined with a view to clear up some points which arose out of the author's previous investigations on liquid mixtures.[9] The first problem was to follow the changes in the inner ring present in associated liquids like acetic acid, on dilution. This point was only partially studied previously. Secondly, the influence of dilution on liquids which showed the presence of two prominent haloes remained to be investigated. These two points have now been studied, using for this purpose (1) acetic acid-water solutions, (2) ethyl phthalate-benzene systems, (3) mesitylene-cyclohexane mixtures.

2. *Experimental Procedure.*

The copper Kα radiation was used as usual as the incident beam. The camera consisted of a wooden box covered with lead sheet and fitted in front with a cylindrical block of lead containing a hole about 0·5 mm. wide along a length of 3 cms. after which it was widened out. A small lead disc suspended by a stiff wire just in front of the photographic plate served to cut out the direct beam. Unless this precaution was taken, the halation produced on the plate by the direct beam was sufficient to mask any effects occurring at small angles. In some experiments, the sharp arcs produced by the X-rays impinging on the sides of the lead disc could be easily made out. The cell for holding the liquid consisted simply of a gold plate, 1 mm. thick with a circular hole in the centre.

Sogani's method of using very thin mica as windows for the cell was found to be very convenient, since mica could be obtained in thin plates, and what is more important, gave rise to only Laue spots which did not in any way interfere with the broad rings given by the liquids. Rubber solution, gum solution or sodium silicate was used for pasting the mica to the cell, preferably the one which was not dissolved by the liquid contained. Ilford Iso-zenith plates were used throughout, and the exposures varied from 2-4 hours. The distance between the plate and the liquid as calculated from a powder pattern of hexamethylene tetramine was found to be 2·45 cms. Blank exposures and patterns of pure distilled water were taken from time to time to see that there was no extra scattering at small angles due to any cause.

3. *Colloidal Solutions.*

All the solutions examined showed the strong small angle scattering, and its nearness to the central beam indicated that the molecular weights were very high. Soluble starch showed, according to a rough calculation, the largest molecular weight. In the case of tannin and gum arabic, the presence of a weak inner maximum even in the dilute solutions pointed to the formation of micelles, and probable values for the sizes of the micelles were obtained. The results are given in the following table, and the pattern of each solution is described later in detail. The proportions refer to parts by weight of solute and solvent respectively. The spacings of the haloes were obtained in the usual way by the application of Bragg's law.

Table I.

Substance.	Inner Ring.		Outer Ring.		Other Rings. λ in A.
	θ in degs.	λ in A	θ in degs.	λ in A.	
Starch, powder	6·1	14·4	17·3	5·13	3·84
Starch, soln. 1:3 and 1:5	up to 4·6	up to 19·0	27·3	3·26	
Tannin, powder	13·8	6·42	24·7	3·60	
Tannin, soln. 1:2	up to 5·3	up to 16·8	26·1	3·41	Very faint, diffuse max. at 6·5 A present.
Tannin, soln. 1:4	,,	,,	26·6	3·35	
Gum Arabic, solid	10·4	8·50	18·1	4·90	
Soln. 1:2	up to 6·8	up to 15·1	17·0	5·21 (faint)	Strong ring at 3·47 A.
Water	...	...	27·5	3·24	

(1) *Starch and solutions.*—Merck's soluble starch was used in these experiments. When made into a paste with the requisite amount of distilled water, and warmed over a flame, it was converted into a translucent jelly which was examined as such. Starch powder gave rise to three fairly sharp rings, the second one with a spacing of 5·13 A being the most prominent. The long spacing was very weak, but the outermost ring was of fair intensity. A 1:3 jelly showed a strong corona extending up to 4°38′ and a very broad and diffuse halo just in the position of the water halo. There was a considerable amount of scattering between the corona and the ring, as well as outside the ring. A 1: 5 solution showed essentially the same features, the corona being, however, less intense, and the scattering within the ring also being less.

A rough calculation of the size of the starch molecule from the small angle scattering gave the following value for the molecular weight :

$$\text{Mol. wt. of soluble starch} = \frac{(19{\cdot}0)^3 \times 1{\cdot}50}{1{\cdot}66} = 6200.$$

This indicates that the starch molecule contains about ten dextrin molecules united together or about 40 glucose residues so united.

(2) *Tannic acid and solutions.*—Merck's extra pure variety was used in the experiments. The pattern for the solid consisted of two rings, the outer one being fairly strong (spacing 3·6A) and the inner one faint and diffuse (spacing 6·4A). A 1 : 2 solution in water gave a pattern which consisted of (1) a strong scattering at very small angles, (2) a very diffuse and faint inner maximum nearly in the same position as in the powder, (3) a broad outer ring which was intermediate in size between the water ring and the outer ring of tannic acid. In a 1 : 4 solution, the outer ring was shifted more towards the water maximum, and the inner ring was barely detectable.

The above observation that even in dilute solutions the rings of tannic acid are superposed on the water pattern, points to the fact that just as in soap solutions studied previously, micelles are present, each consisting of a number of simple molecules. A calculation of the size of the micelle was made from the extent of the small angle scattering, taking the density of tannin as 1·097.

$$\text{Mol. wt. of tannin} = \frac{(16{\cdot}8)^3 \times 1{\cdot}097}{1{\cdot}66} = 3134.$$

Since the formula of tannin is $C_{14}H_{10}O_9$ with a molecular weight of 322, it follows that each micelle contains nearly ten simple molecules united together. This fact is in harmony with osmotic pressure data which show that the actual unit is much larger than that indicated by its chemical formula.

The mol. wt. indicated by the osmotic pressure measurements is 273,* and is of the same order as that obtained here.

(3) *Gum Arabic.*—The sample used consisted of some clear pieces picked out of the commercial variety. A small piece about 1 mm. thick was directly examined, and the pattern showed a faint inner ring and a stronger outer one (spacing, 4·9A). A 1 : 2 solution showed the same features as in the case of tannin, *viz.*, a strong scattering at small angles, a faint and diffuse ring nearly in the same position as the prominent one for the solid, and an outer ring which was slightly smaller than that for water. The presence of micelles was therefore indicated in this case also. The mol. wt. was calculated in the usual way :

$$\text{Mol. wt. of gum arabic} = \frac{(15{\cdot}1)^3 \times 1{\cdot}355}{1{\cdot}66} = 2810.$$

This is of the same order as the molecular weight determined from osmotic pressure measurements which has a value of 1750.

4. *Liquid Mixtures.*

(1) *Acetic acid and solutions.*—The pure acid showed a faint inner ring and a strong outer one. There was also some general scattering within the rings. Even the addition of a little water (4 : 1 solution) was found sufficient to convert the inner ring of acetic acid into a strong general scattering in the same region. The outer ring in this case was only slightly more diffuse than that of the pure liquid. The assumption that the inner ring in pure acetic acid is due to molecular association** indicating a separation of two molecules placed together end to end is hence quite justified since that arrangement is quickly destroyed by dilution. A 2 : 1 solution showed a gradual broadening of the single halo present in the direction of the water halo. The scattering within the ring was strong in this case also. At 1 : 2 dilution, the ring had broadened out further, and the inner scattering too had diminished.

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* E. F. Burton, " The Physical Properties of Colloidal Solutions, " p. 122 (1916).

** Krishnamurti, Ind. J. Phys., 2, 491 (1928).

TABLE II.

Liquids.	Inner Ring.		Outer Ring.	
	θ in degs.	λ in A.	θ in degs.	λ in A.
Acetic Acid, pure	12·1	7·30	21·2	4·19
Soln , 4 : 1	...	...	22·2	4·00
„ 2 : 1	...	...	22·7	3·91
„ 1 : 2	...	...	25·3	3·51
Water	...	...	27·5	3·24

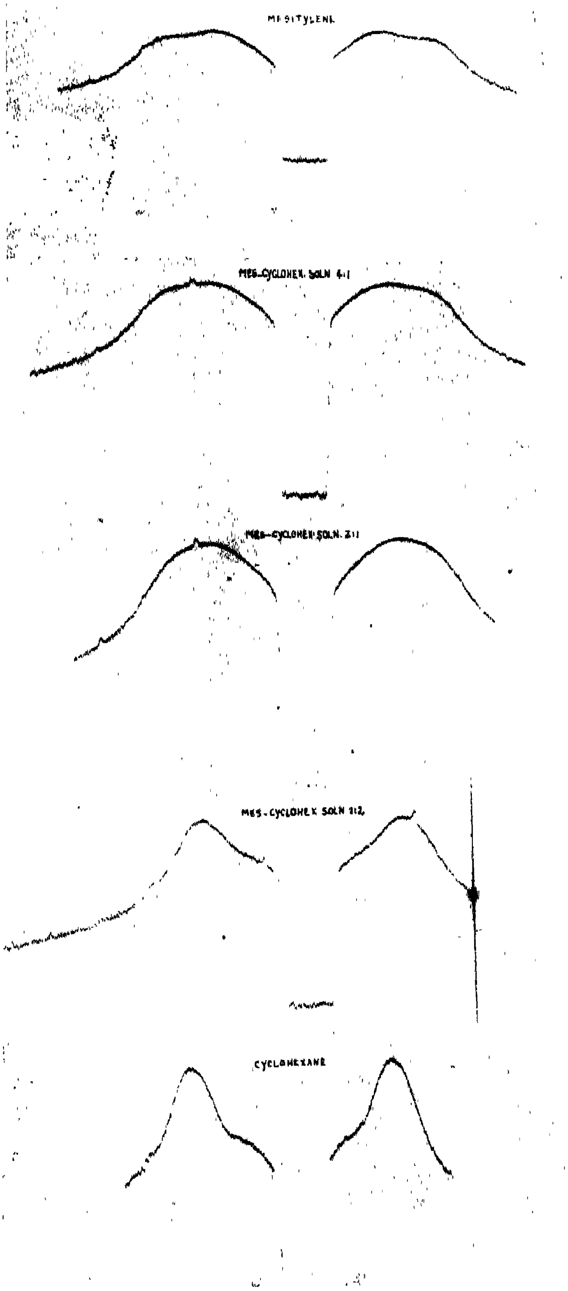
(2) *Ethyl phthalate-benzene mixtures.*—Ethyl phthalate in the pure state showed two rings of about equal intensity which were clearly separated from each other (spacings 7·10 A and 4·10 A), while pure benzene gave a halo with a spacing of 4·76 A. A concentrated solution (3 :1) showed the inner and outer rings of ethyl phthalate in about the same positions, but there was now greater amount of scattering between the two rings. In a 2 :1 solution, the inner ring had weakened, but its position was the same as before. The outer ring had become more diffuse, and the separation between the two rings was not clear. At 1 :1 dilution, the inner ring had given place to a general scattering, and the outer ring was nearly of the same size as the benzene ring, though considerably diffuse. A 1 :2 solution showed less internal scattering, though the latter was still larger than that in pure benzene.

TABLE III.

Liquid.	Inner Ring.		Outer Ring.	
	θ in degs.	λ in A.	θ in degs.	λ in A.
Ethyl phthalate	12·4	7·10	21·7	4·10
Soln., 3 :1	12·1	7·30	20·2	4·40
„ 2 :1	12·1	7·30	19·7	4·51
„ 1 :1	...	...	19·1	4·57
„ 1 :2	...	...	18·6	4·76
Benzene, pure	...	...	18·6	4·76

The results showed that at greater concentrations the solute molecules are oriented in much the same way as in the pure liquid. But at 1 : 2 and larger dilutions this does not hold good since the inner ring of ethyl phthalate was no longer present, but only a general scattering instead. In 1 : 2 and more dilute solutions, there is almost random distribution of ethyl phthalate molecules in benzene. The two essential features in the different patterns of increasing dilution, *viz.*, the joining together of the outer ring of ethyl phthalate with that of benzene, the disappearance of the inner ring of ethyl phthalate and the appearance of a general scattering at small angles, are in harmony with the conclusions arrived at above.

(3) *Mesitylene-cyclohexane mixtures.*—Cyclohexane was chosen as solvent because it gave a rather sharp ring with very little scattering inside it. The changes in the patterns on dilution followed in general the same lines as in the case of ethyl phthalate-benzene mixtures. The pattern for pure mesitylene consisted of two rings, the inner one being slightly stronger than the outer. Considerable scattering was present between the two rings. The spacings of the two rings were 6·2 A and 4·1 A respectively while that of pure cyclohexane



Microphotometer curves

X–Ray Diffraction by Mesitylene–Cyclohexane Mixtures

was 5·1 A. Even in a very concentrated solution (4 : 1) the two rings of mesitylene could not be distinguished separately, and they were considerably broadened out and diffuse. In a 2 : 1 solution, the outer portions of the single broad halo were very diffuse and faint. There was also a large scattering within the ring. A 1 : 2 solution showed only the cyclohexane ring slightly broadened out together with a fair amount of scattering within the ring. The microphotometer curves showed these changes very clearly. The values for the diffraction maxima given in the following table have been measured from the microphotometer curves.

TABLE IV.

Liquid.	Inner Ring.		Outer Ring,	
	θ in degs.	λ in A	θ in degs.	λ in A.
Mesitylene, pure	14·3	6·19	21·8	4·07
Soln., 4 :1	14·9	5·92	20·8	4·28
,, 2 :1	16·1	5·51	...	...
,, 1 :2	17·3	5·11	...	...
Cyclohexane, pure	17·3	5·11	...	...

It seems probable from the results that there is greater amount of superposition in these solutions than in the previous case, which persists to greater dilutions. This can probably be ascribed to the disc-shaped structure of the mesitylene molecules, which enables them to maintain a very approximate arrangement in fairly concentrated solutions. This disappears rapidly with increasing dilution when the solute molecules are more and more randomly orientated.

The relationship deduced by Raman and Ramanathan[2] that the pattern for the mixture should be essentially a superposition of the patterns of the constituents is valid only when the two kinds of molecules are similar in shape and size (*e.g.*, *o*-nitrobenzaldehyde and methyl salicylate mixtures). When these two factors change, as is usually the case we get as an extreme case patterns like those of dilute sugar solutions where the solute molecules are distributed at random in the solution. Superposition is also observed when micelles are present in the solutions. The patterns in all the other cases indicate intermediate stages of arrangement.

5. *Summary.*

1. Aqueous solutions of starch, tannic acid and gum arabic showed a strong scattering at small angles to the primary beam, due to the dissolved molecules or micelles. The molecular weights calculated from the extents of the coronae were 6200, 3134 and 2810 respectively.

2. The inner ring in acetic acid disappears even in very concentrated aqueous solutions, indicating a breaking up of association.

3. Mesitylene-cyclohexane and ethyl *o*-phthalate-benzene systems showed changes in the patterns which could be interpreted as due to greater randomness of orientations of the solute molecules with increasing dilutions.

BIBLIOGRAPHY

(1) Wyckoff, Amer. J. Sci. *5*, 455 (1923).
X-ray diffraction effects from liquids and liquid mixtures.

(2) Raman and Ramanathan, Proc. Ind. Assn. Cult. Sci., *8*, 127 (1923).
Theory of X-ray diffraction in liquids, solutions and amorphous solids.

(3) Katz, Proc. Roy. Soc. Amst., *27*, 505 (1924).
X-ray researches on the nature of swelling phenomena.

(4) Katz and Mark, Proc. Roy. Soc. Amst., *27*, 520 (1924).
X-ray investigations on the nature of swelling.

(5) Debye, Phys. Zeit. *28*, 135 (1927).
Theory of X-ray diffraction by amorphous bodies.

(6) Krishnamurti, Ind. J. Phys., *2*, 501 (1928).
X-ray diffraction in solutions.

(7) Krishnamurti, Ind. J. Phys. *3*, 209 (1928).
The diffraction of X-rays by solutions of canesugar, levulose and glucose.

(8) Krishnamurti, Ind. J. Phys., *3*, 307 (1928).
On the nature of dextrin, gelatin and sodium oleate solutions by X-ray diffraction.

(9) Krishnamurti, Ind. J. Phys., *3*, 331 (1928).
X-ray diffraction by liquid mixtures.

(10) Prins, Nature, Jan. 19, 1929.
Diffraction of X-rays in liquids containing heavy atoms.

(11) Krishnamurti, Ind. J. Phys., *3*, 507 (1929).
X-ray diffraction in solutions and the molecular structure factor.

(12) Hertlein, Z. f. Phys., *54*, 341 (1929).
The diffraction of X-rays in liquids and liquid mixtures.

(13) Debye, Bewilogua and Ehrhardt, Phys. Zeit., *30*, 84 (1929).
Diffraction of X-rays by simple molecules.

(14) Shiba and Watanabe, Sci. Rep. Inst. Phys. Chem. Res. Jap., *10*, 187 (1929).
X-ray diffraction haloes in aqueous solutions of electrolytes.

(15) Hirata, Bull. Inst. Phys. Chem. Res. Jap., *8*, 471 (1929).
X-ray diffraction by " Midu-Ame."

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X-Ray Diffraction in Heated Liquids and in Solutions

By

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(Plates XVI, XVII and XVIII)

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ABSTRACT.

The scattering of X-rays by a number of liquids has been examined at high temperatures. The general effects observed are an increase in the scattering at small angles, diffuseness and contraction of the haloes with rise of temperature. The scattering at small angles in the case of benzene increases in the ratio of 1:3;9 at 25°, 100° and 210°, comparable with that observed in the scattering of light (1;2;4 approx.).

The ratio of the intensity of the X-ray scattering at small angles by unit volume of the liquid to that of the primary beam in the case of water and benzene are 3×10^{-6} and 1.3×10^{-6} respectively at 25°C. This is in fair agreement with the theoretical value 2.1×10^{-6} and 1.1×10^{-6} calculated according to the Einstein-Smoluchowski formula applied to X-rays by Raman and Ramanathan (Proc. Ind. Assn. Cult. Sci., 8, 129 (1923).

The broadening and diffuseness of the haloes were studied in the case of associated liquids like phenol, propionic acid, caproic acid, etc. Of the two haloes present, the intensity of the inner one was not found to diminish to any marked extent even at moderately high temperatures. This is interpreted to mean that their origin is not primarily due to the association of the molecules, but depends on the state of the liquids determined by the form of the molecules and by their electrical polarity. In the case of ethyl orthophthalate, O-nitrobenzaldehyde and tetranitromethane, the thermal effects especially on the outer maxima were comparatively small.

The scattering at small angles in dilute aqueous solutions of cane sugar and glucose were examined quantitatively. In a 1 : 3 solution of cane sugar and glucose the ratio I/I_0 was 1.2×10^{-6} in the former and nearly e 0.8×10^{-6} in the latter, where I is the intensity of scattered and I_0 of the incident radiation. Considering the dissolved molecules as small isotropic dielectric spheres randomly distributed in water, it is shown theoretically that at an angle of nearly 4 degrees with the primary beam where the intensities are compared, the respective values are 3.1×10^{-6} and 1.8×10^{-6}.

1. *Introduction.*

As early as 1923, Raman and Ramanathan[1] put forward a theory of X-ray diffraction in liquids, which explained in a remarkable way the scattering at small angles to the primary beam, and the presence of one or more maxima at larger angles. It was shown by the authors that the Einstein-Smoluchowski theory of optical scattering is applicable as it is to small angles of scattering in the case of X-rays, and so the ratio of the intensity of the scattered to that of the incident beam must be the same as in optics, and should further show a considerable increase at high temperatures. The object of the present investigation is to test the above predictions of the Raman-Ramanathan theory. Does the increase obey the optical scattering law ? How far does the absolute value of the intensity of the radiation scattered at small angles conform to that expected according to the Einstein-Smoluchowski theory in the optical region ? The following experiments have been carried out to find an answer to these questions.

Preliminary investigations were made on the subject by the author[2] and Ramasubramanyam[3] in a few liquids. In the present experiments numerous liquids are examined qualitatively at high temperatures and quantitatively in one case. Another important object that has been kept in view, is to follow the changes of the inner haloes with rise of temperature in cases where two haloes are present. It has been suggested by different authors that these haloes are due to the presence of associated double molecules and it was expected that the investigation of the thermal effect would enable us to understand if this is the case.

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[1] Raman and Ramanathan, Proc. Ind. Assn. Cult. Sci., **8**, 129 (1923).

[2] Vaidyanathan. Ind. Jour. Phys., **3**, 391 (1929).

[3] Ramasubramanyam, Ind. Jour. Phys., **3**, 127 (1928).

The increase in the scattering at small angles has also been observed with dilute solutions of various substances, notably the sugars. The effect has been attributed to the randomly distributed molecules of the dissolved substance. It was, therfore, considered desirable to examine quantitatively this increase of intensity in dilute solutions.

The experimental arrangements were similar to those employed in the previous work. The distance between the cell and the photographic plate was 4.0 cms. in the thermal experiments. The incident beam consisted of copper K radiation as in the previous work which was cut out by means of a suitable lead disc suspended just in front of the plate.

The technique for obtaining higher temperatures was improved and the photographs obtained were more satisfactory than in the previous investigations. The plates were microphotometered in many cases to make the investigation more quantitative. (A Moll microphotometer constructed by Messrs. Kipp and Zonen was employed.) Other details of the quantitative estimations are described under different sections.

2. *Remarks on the Liquids Studied.*

Before proceeding to describe the thermal effects, a very short description may be given of the general nature of the haloes and microphotometer curves of the liquids at room temperature. All the liquids examined have two haloes but tetranitromethane has three. Fused silica (solid) also possesses two haloes. Most of the liquids were known to possess two maxima from the work of previous experimenters and have been specially selected for investigating the influence of heat on the inner haloes * which as pointed out, is highly important. Cyclohexene and cyclohexanone do not seem to have been investigated previously. It may be pointed out that these liquids and benzene as well possess diffuse inner maxima. An idea of the relative sharpness of the haloes can be obtained from the plates and the microphotometer curves. But comparatively, the outer haloes of diphenylamine and phenol are sharper. The inner halo of phenol is also well-defined and clear. In the case of ethyl orthophthalate and O- nitrobenzaldehyde the inner haloes are larger than was usually observed in other liquids examined here and they are slightly more intense than the outer maxima.[1] In the case of tetranitromethane, the outermost maximum is relatively fainter than those of the two other liquids and it has some resemblance to the faint outer maximum in carbon tetrachloride.[2]

There is a large amount of scattering within the region of the haloes in almost all liquids and in the microphotometer curves, the maxima appearing as large humps placed in this general scattering. Outside the primary halo the curve gradually slopes down but throughout the region of the photographic plate, outside the maximum there is a scattering of about 5% of that at the halo. At small angles

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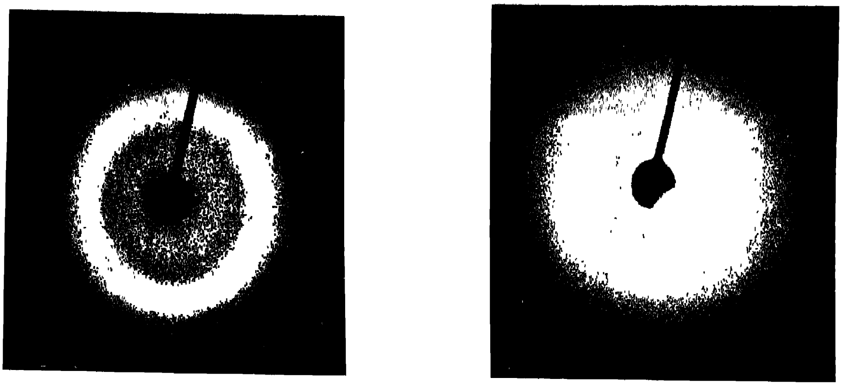
* Acetic & butyric acids & ethyl alcohol have already been examined by the author (*loc. cit.*).

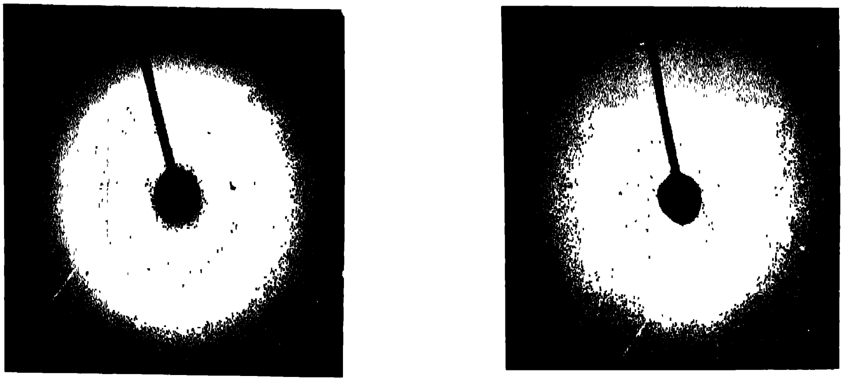
[1] Krishnamurti, Ind. Jour. Phys. 2, 355 (1928).

[2] Sogani, Ind. Jour. Phys., 2, 371 (1928).

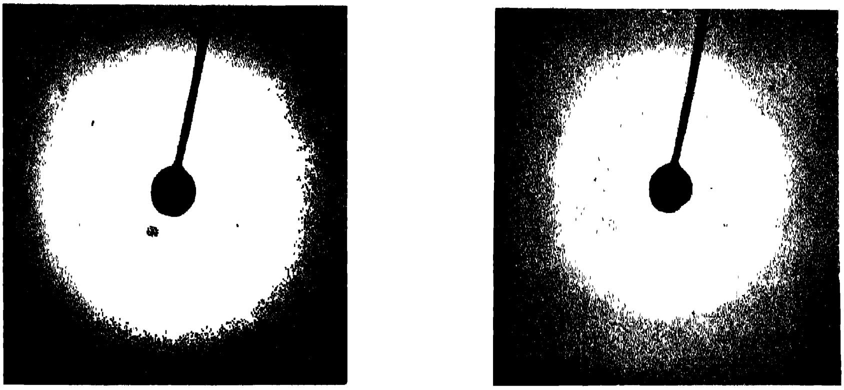
Cold Hot



Cyclohexene



Phenol



Caproic Acid

X–Ray Diffraction in Heated Liquids

with the primary beam *i. e.* just outside the central disc in our arrangement and making an angle of about 3.5 degrees withe the central beam, the intensity of scattering shows a rapid decrease, but the important point to observe is that the intensity is larger than in the regions outside the maxima[1]. It is however necessary also to remark that the shape of the microphotometer curve depends on the magnification employed in it (1 mm. of the plate corresponds to 7 mm. along the abscissa of the curve). The sharpness of the maxima and minima depends on the volume of the scattering material, the width of the incident beam and the blackening of the photographic plate. In the present case, the radius of the incident beam of X-rays was 0·7 mm. at the cell and that of the glass containers 0·75 mm. approximately.

3. *Influence of Temperature.*

On heating the liquids the X-ray haloes undergo remarkable changes in many cases. The general effects are that at small angles (very near the central disc) the intensity increases considerably with rise of temperature ; the maximum becomes flattened and diffuse; the clear space separating the inner and outer haloes becomes filled up and the haloes contract.

The results are shown in Table I. In this table, a_1 corresponds to the primary maximum and is the spacing calculated according to Bragg's law, a_2 is the inner maximum and a_3 the outermost one. The symbols d, s.d. and v.d. stand for diffuse, slightly diffuse and very diffuse respectively.

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[1] See also Hewlett, Phys. Rev. 20, 688 (1922).

TABLE I.

Liquid	Temperature	a_1	a_2	a_3
Cyclohexanone	25 195	5·3 6 (d)	10 v.d.	
Terpineol	23 195	5·3 6·5 (d)	10 v.d.	
Cyclohexene	25 165	4·9 5·7 (d)	10 v.d.	
Benzene	25 210	4·80 5·4 (v.d.)	11 (d) washed off	
Phenol	27 120 210	4·81 5·0 5·3 (d)	9·5 9·9 v.d.	
Diphenylamine	60 195	4·6 5·0 (d)	9 4 v d.	
Propionic acid	25 155	4·43 4·93	8·0 9·6 s.d.	
Acetonitrile	25 135	4·21 4·41	8·7 s.d.	
Ethyl O-phthalate	25 235	6·71 7·0 (s.d.)		4·2 4·0
O-nitro benzaldehyde	50 160	6·41 6·7 (s.d.)		3 8 4·0
Tetranitromethane	25 110	5·52 6·0	10 s.d.	3·06 s.d,
Fused Silica	25 250	4·98 Slight contraction	8·9	
Octane	25 150	4·62 4·85 (s.d.)	v.d. v.d,	
Pentane*	30 92 122	4·85 5·00 5·22		
Caproic acid	30 160	4·59 4·76	12·9 14·0 s.d.	

The results for pentane are those of Ramasubramanyam *loc. cit.*

The thermal effects vary widely for different liquids and so they are presented in some detail pointing out the essential features and differences. For purposes of convenience in description they may be classed as follows :—

1. *Benzene*[1] *and cyclohexene.*—The haloes of these two liquids become completely washed off at about 200°C, but there are traces of the outer halo in cyclohexene. This has been heated only to 165°C, whereas benzene has been raised to 210° (critical temperature of benzene is 280°). The scattering continuously increases towards small angles more or less as in the case of gases. (See microphotometer curve for benzene, plate for cyclohexene.) On a close examination however there is a faint hump in benzene also, about the position of the primary maximum.

2. *Phenol, diphenylamine, terpineol and cyclohexanone.*—The effects are comparable to those of benzene and cyclohexene, though slightly smaller. The haloes could be distinguished in the hot patterns, the inner as well as the outer. Relatively the inner ones have become much more diffuse than the outer.

Phenol was examined at 25°, 120° and 210°C. At 120°C both the haloes are clear, though more diffuse than at 25°C. Compared with phenol and terpineol the inner haloes in diphenylamine and cyclohexanone are faint and diffuse even in the cold patterns and have become more so in the hot ones. All of them were heated to 220°C to compare the effects with benzene. The clear space that separates the inner and the outer maxima at high temperatures is much less clear than in benzene, but still considerable.

It is important to observe that though the inner haloes have become diffuse, they are not completely washed off as in benzene. When the haloes are very diffuse it is difficult to locate the peaks of the maxima and the spacings given are correspondingly less accurate.

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[1] A quantitative examination has been made of the increase in intensity of scattering at small angles in benzene and is described in a subsequent section.

3. *Propionic acid and acetonitrile.*—These have been heated to 155 and 135°C. The diffuseness and the increase in internal scattering are less striking. In propionic acid, both the haloes can very clearly be seen in the hot patterns though contracted. In acetonitrile, the inner halo is faint and diffuse in the cold but can still be seen distinctly in the hot pattern.

4. *Ethyl O-phthalate and O-nitrobenzaldehyde.*—The former liquid has been maintained at 235° but the thermal effects are much less striking than in those liquids mentioned above. The outer maximum has contracted even less than the inner. As previously mentioned, the inner maximum in this liquid is more intense than the outer.

So far as the thermal effects are concerned the same remarks apply to o-nitrobenzaldehyde, but this has been heated only to 165°.

5. *Tetranitromethane.*—At room temperatures this has been investigated by Krishnamurti[1] who has observed the primary and the outer maxima. The liquid also possesses a faint inner maximum. At a temperature of 120° beyond which it was impossible to maintain the liquid, for it invariably decomposed with explosive violence, the haloes were found to contract. The contraction of the outer maximum is comparatively very small, but its faint hump in the microphotometer curves is not so prominent in the hot as in the cold.

6. *Silica.*—An attempt was made to heat silica in the form of a thin tube to a very high temperature, but the experimental difficulties such as the melting of the lead in the camera and fogging of the plate prevented the same. So far as could be learnt from the negatives up to 250°, no striking effect was observed. It is also worthy of remark that the halo at small angles is stronger in silica than the outer.[2]

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[1] Krishnamurti, Ind. J. Phys., 3, 507 (1929).

[2] The author is not aware of any previous work on fused silica.

7. *Caproic acid and octane.*—As typical of long chain aliphatics, these two liquids were examined. Caproic acid was heated to 160°. The haloes contracted, but did not become appreciably diffuse. The relative intensity of the inner halo was almost the same as in the cold, but more diffuse. At the same temperature the halo for octane showed a larger diffuseness.

4. *Quantitative Study with Benzene.*

A quantitative investigation has been made of the increase in intensity at small angles, in benzene. The arrangement and the results are presented below.

The camera is fitted in front with a "Compur" shutter, the leaves of which are of lead. When the liquid is exposed, the lower half of the film is kept screened with a lead sheet and the X-ray tube operated as steadily as possible for a known period (about 5 hours). After the exposure, the lead plate is moved up and the lower half exposed to a series of graded exposures from a fraction of a second to two seconds. The plate is then developed[1] and the series of spots obtained and the scattered spectra are microphotometered.

Similar experiments are carried out at high temperatures. These exposures are exceedingly troublesome and also liable to sources of error which are mentioned subsequently.

It will be seen from the curves that the ordinate of the microphotometer spectrum of benzene at 25° at small angles, is comparable to that of a 1/10 second direct exposure, whereas in the hot pattern, the corresponding height is nearly equal to that of one second. The cold exposure (25°C) of benzene was 6 hours and hot (210°C) 5 hours.

The mean value of a few observations after small corrections, gives 1 :3 :9 (to the nearest integer) for the relative intensities of scattering at small angles for benzene at 25,100 and 210°C.

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[1] "Photographic Photometry" by Dobson Griffith and Harrison, Clarendon Press, 1926.

5. *Absolute Intensity of Scattering.*

The method adopted was similar to that in the previous section, but here it is necessary to know the volume of the scattering element, the divergence of the beam of X-ray and also the absorption of X-rays by the liquid and the cell.

In the direction of the X-ray beam, the length of the scattering element is the thickness of the cell. The area of cross section in the plate at right angles to the beam was determined by giving an instantaneous exposure on a film placed at the surface of the cell. The divergence of the beam could be known by giving a similar exposure at the distance of the photographic plate; the relative areas of the patches being a measure of the same. There is some difficulty in measuring the latter area, for the patch is diffuse at the edges and slightly different in area for different exposures.

The correction for absorption was made both theoretically and experimentally. The results given are when the beam passes through the liquid.

Taking now the case of water, it will be seen from the microphotometer curves that the height at small angles in the case of water[1] is between that for 1/25 and 1/10 second exposure to the direct beam. Computation from a smoothed curve indicates nearly 1/15 second to have the corresponding intensity. The liquid was exposed for 4 hours. The relative areas of the patches corresponding to the divergence of the beam, as described previously are in the ratio of 1 : 4. This gives $1{\cdot}3 \times 10^{-6}$ for $\frac{I}{I_0}$ at 25° for water.

Similar experiments were made for benzene and the absolute intensity $\frac{I}{I_0}$ was nearly 3×10^{-6} at 25°C.

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[1] It is important to remark that water has two haloes corresponding to spacings 8·8A. and 7·0A. This does not seem to have been observed by previous investigators. The inner halo is very faint and diffuse.

6. *X-Ray Scattering in Solutions.*

Aqueous solutions of four different concentrations of cane sugar and glucose respectively were quantitatively examined for the increase in intensity at small angles. The method adopted was the same as in the determination of the intensities in liquids. The same camera as for water was employed for solutions. When the intensity of scattering due to water itself ($1{\cdot}1 \times 10^{-6}$) is subtracted from that of the solution, the excess gives that due to solute molecules.

In 1:3 and 1:5 by weight of cane sugar the increase in intensity was $1{\cdot}2 \times 10^{-6}$ in the former and nearly the same in the latter. In the same concentration by weight of glucose the intensity was $0{\cdot}8 \times 10^{-6}$ in 1:3 and feebler in the 1:5. Increases in intensity of scattering at small angles have been qualitatively observed in many solutions previously.[1] In 1:3 solution of cane sugar in addition to the increase in intensity there is also a halo at about 12^{0} (i.e.) approximately in the position of the inner halo of water (remarked previously) the intensity has slightly strengthened. [Cane sugar powder has a strong halo at $12{\cdot}2^{0}$]. In a 1:5 solution the halo at this angle was the same as the inner halo of water, the latter one being extremely faint. In these solutions there was no striking change on the primary halo of water with the spacing of 3·3 A.U.

7. *Experimental Precautions and Sources of Error.*

In measuring the intensities, the tube has to be operated continuously from 4 to 6 hours under steady conditions and this is only approximately possible. The instantaneous exposures depend on the periodicity of the interrupter and for short intervals of a small fraction of a second, the proportionality with time cannot be taken as very accurate, since the variations in the number of interruptions begin to influence the same.

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[1] Krishnamurti, *loc. cit.*; Watanabe, Sci. pap. Inst. Phys. Chem. Res., **183. 187, 1929.**

The sensitiveness of the different parts of the film varies slightly. Eastman Kodak X-ray films were employed and these were found very satisfactory. The density of the image is proportional to the logarithm of the intensity of the radiation and hence the difference in intensity between the graded exposures is small.

The patches obtained on the plate by giving instantaneous exposures are diffuse at the edges, being slightly less intense there than in the middle. This error is rectified to a very great extent by the microphotometer for the length of the small beam of light that falls on the film gives the average effect.

There is also the question of dovelopment[1] but since the same plate is used, this does not influence the relative intensities.

Copper anticathode was used and the potential was regulated to minimise the admixture of harder radiations.

The halation round the central disc is tested by giving blank exposures, and the regions for comparison are chosen so remote as not to be vitiated by the same. A sufficiently large lead disc is used in front when liquids are exposed, but it may be pointed out that it is not possible to entirely free the regions at very small angles from the source of error. It also increases when a wide beam is used. The controlling of these conditions is a matter of experience.

In the experiments on thermal effect, the halo of the glass container is a difficulty, for it has to be thick enough to withstand the pressure. Different specimens of glass were tried and all of them gave two haloes. In pyrex however the inner halo was exceedingly faint in the blank exposures and

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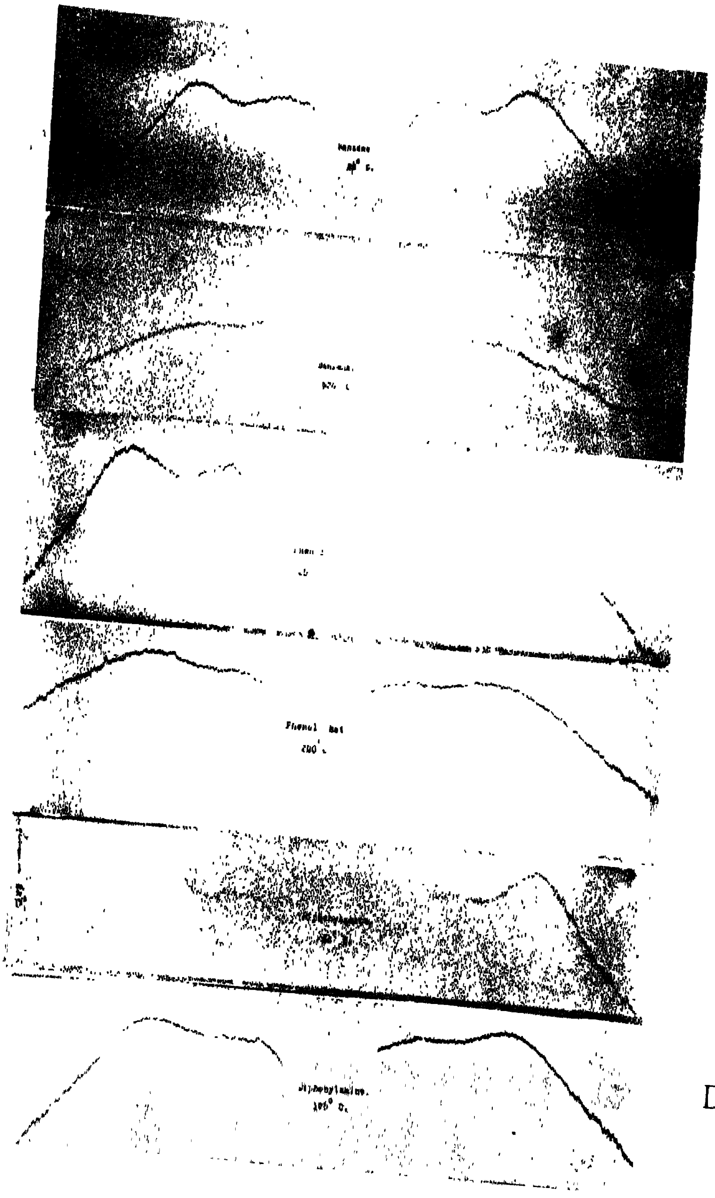
[1] Dobson, Photographic Photometry.



Benzene
25° C

Benzene
220° C

Phenol
25° C

Phenol
220° C

Diphenylam
60° C

Diphenylam
195° C

X-Ray Diffraction in Cold and Hot Liquids
Microphotometer Records

so thin pyrex tubes were invariably employed as containers. In the case of liquids at different temperatures, the relative effects are not vitiated by the glass haloes, for the latter do not undergo any alteration during heating. A mica cell was however used as the container for water and solutions.

The various sources of error mentioned in this section have been avoided as far as possible.

8. *Comparison of Experiment and Theory.*

Of the various phenomena, the most important is the increase in the scattering at small angles on heating the liquids and the agreement of the absolute value of the intensity of the scattered radiation at small angles, considering it similar to the optical case. These facts have been predicted by Raman and Ramanathan.[1]

It is of great importance from the thermodynamical stand point, that in the region of X-rays also, a medium can be considered as a structureless continuum under appropriate conditions and that the experiment and theory are in accordance with the same. The simple treatment of Raman and Ramanathan [1] depends on the possibility of dividing up a medium into slabs of thickness $\lambda/2 \sin \frac{\theta}{2}$ which can further be subdivided into several slices, each of which is many molecules thick, so that the fluctuations of density in any slice can be assumed to be independent of those in neighbouring ones. This in general is obviously possible only when λ is large, which is true in the optical case. When λ is comparable with molecular dimensions and has any moderate value, each slab of thickness $\lambda/2 \text{ Sin } \frac{\theta}{2}$ would be only a few molecules thick, and it would no longer be possible to assume that when it is subdivided into thinner slices, the fluctuations in different slices are uncorrelated *i.e.* independent of each other. In fact it is easy to see that when the volume of the liquid is divided into very thin slices, each only a molecule or so in thickness, any excess of density in one slice necessarily involves a deficiency in the adjoining slices and *vice versa.* The simple summation of intensities of the scattered waves due to the intensity fluctuations in the different slices thus ceases to be admissible.

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[1] Raman and Ramanathan *loc. cit.*

In one case however the Einstein-Smoluchowski theory may be applied as it stands to the problem of X-ray scattering. This is when the angle of scattering is very small. The thickness $\lambda/2 \sin \frac{\theta}{2}$ of the slabs is then appreciable and may be made as large as we please, by sufficiently decreasing θ. For instance if $\lambda = 1.54$ A.U. and $\theta = 10'$ of arc, each slab would be 120 molecules thick and this thickness should be ample to enable the Einstein—Smoluchowski theory to be applied. Even for an angle of 3 degrees, a layer would be about 15 molecules deep and though the Einstein-Smoluchowski theory would not be strictly valid, it should nearly hold good.

At very high temperatures as observed in benzene, the intensity tends to be larger than in the optical region. For according to the observations of Ramachandra Rao[1] the intensities of scattered radiation in benzene at 20, 100, 220°, are in the ratio of 0·96:1·6:3·4 in the optical region. The deviation at very high temperatures in the case of X-rays is possibly due to the contribution from the diffuseness of the haloes. For if the haloes have become completely flattened out, the diffuse edges will superpose on the optical scattering and since the comparison is made at definite angles, however small, this contribution tends to increase the observed value.

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[1] Ramachandra Rao. Ind. J. Phys., 3, 21 (1928).

When we consider the question of those liquids like propionic acid, ethyl o-phthalate, etc., the smallness of the increase in internal scattering follows from the small increase in compressibility. For it is well known that the compressibility increases rapidly, only near the critical temperature, and in liquids having very high critical temperature, striking increases cannot be expected. Benzene and cyclohexene have a low boiling point and critical temperature whereas phenol, ethyl o-phthalate etc. have a high boiling point and critical temperature. There is a difficulty that occurs in liquids having strong inner haloes at very small angles and this prevents a quantitative estimate. But the general observations on different liquids and the quantitative estimate in benzene, bear out the expectations of the optical theory in a remarkable manner.

The absolute value of the intensity I/I_0 in water and benzene can also be calculated according to the formula

$$I/I_0 = \frac{\pi^2 kT\beta\,(\mu^2-1)\,(1+\cos^2\times)v^2}{2\lambda^4 r^2}.$$

The letters have the usual significance. μ is the refractive index of water for X-rays of wave length 1·54A. and is equal to 1-3·58 x 10^{-6} at room temperatures. v is the volume of the scattering element and is equal to $1{\cdot}7\times10^{-3}$ c.cs. The distance of the photographic plate from the cell is equal to 4·7 cms. Taking the forward direction, calculation gives $1{\cdot}1\times10^{-6}$ for I/I° at 25^c C for water. Similar calculations for benzene show I/I° to be equal to $2{\cdot}1\times10.^{-6}$

Taking into account the various sources of error in the experiment, these are in fair agreement with the experimental values, $1{\cdot}3\times10^{-6}$ and 3×10^{-6} for water and benzene respectively.

The expectations of the fluctuation theory of Raman and Ramanathan for X-ray scattering at small angles are thus in accord with the results.

9. *The Origin of the Inner Haloes.*

The diffuseness of the primary haloes, in relation to the theory of Raman and Ramanathan [1] has been discussed in the previous paper [2] and in that of Ramasubramanyam. [3] In the present discussion we shall mainly confine our attention to the thermal effect on the inner haloes and its relation to the primary haloes. Such inner haloes are observed in many liquids ; they are generally faint and being at small angles, are difficult to observe except when they are fairly intense. As pointed out in the introduction, the important question that arises in this connection is, are these haloes purely the results of molecular association as has generally been supposed or do they depend also on other properties of the liquid? When associated liquids like phenol, propionic acid, caproic acid, acetonitrile, etc., are maintained at moderately high temperatures, the intensities of the inner haloes are not found to diminish as would be expected if they were due to association. The temperatures are sufficiently high and near about their boiling points and it is well known that association diminishes greatly at those temperatures. The critical temperatures of these liquids are over 350°C excepting acetonitrile, which has its critical temperature at 270°C. It is only at temperatures far above their boiling points, thermodynamical effects are expected to set in, the inner haloes become more diffuse than the primary, but they are not completely washed off. This behaviour suggests a close relation between the primary halo and the inner.

As could be observed, the inner haloes appear relatively to be extremely faint and diffuse even at temperatures at which the primary haloes could be seen distinctly because of their larger intensity, as for instance in phenol, diphenylamine, terpinol etc., at 200°. Thus in liquids having a low critical temperature as acetaldehyde (191°C), benzene (280), hexane,[1] octane,[2] etc., the room temperature is sufficiently near the critical temperature and due to the thermal agitation, the inner haloes are absent or too faint to be observed. But in nonpolar liquids having high critical temperature or boiling point as for instance mesitylene[3] (367°·7), triethyl benzene[4] the inner haloes are fairly intense. The nonpolar liquids examined are relatively few, compared with polar ones.

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[1] Raman and Ramanathan *loc. cit.*

[2] Vaidyanathan *loc. cit.*

[3] Ramasubramanyam *loc. cit.*

There is also a second factor, namely the shape of the molecule. In long or thin molecules the arrangement of the diffracting planes along the length of the molecule has obviously a smaller chance than a diameter to diameter arrangement. The corresponding haloes, as for instance, in benzene, octane, and other hydrocarbon paraffins, are weak or absent.

But when the molecules are also polar, because they tend to arrange in virtue of their electrical polarity the influence of thermal agitation is felt less than in nonpolar liquids. The distribution is consequently more regular. In addition that the molecular form has a profound influence is also shown from many cases. Flat polar molecules like phenol, ortho-nitrobenzaldehyde or ethyl phthalate have more intense inner haloes than caproic acid, geraniol[5] etc., which are comparatively long.

The contraction of the inner haloes at moderately high temperatures in the same manner as at the ordinary, is very difficult to reconcile with the idea that they are due to the existence of double molecules. In the latter case a pronounced decrease is observed in the intensity and not a contraction that might be expected.

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[1] A faint diffuse halo is observed by Krishnamurti for this liquid. Ind. Jour. Phys. 2, 492 (1928).

[2] A faint diffuse halo is observed in the present investigation, also in octane.

[3] Sogani, Ind. Jour Phys. 2, 97 (1927). See also Stewart, Phys. Rev. (1929).

[4] Katz and Selman. Zeit. fur. phys. 46, 362 (1928).

[5] Vaidyanathan, Ind. Jour. Phys. 3, 371 (1929).

In polar and non polar liquids, each molecule is to be considered as a separate diffracting centre and it is not possible to follow up the process of dissociation with temperature in the case of liquids from the X-ray haloes.

But when the critical temperature, the form of the molecule and the electrical polarity are known, the intensity and the size of the inner haloes can be qualitatively predicted.

10. *The Origin of the Outer Rings.*

In the case of ethyl o-phthalate, orthonitrobenzaldehyde and tetranitromethane, the thermal effects, especially on the outer maxima are very small. This may be due to two causes. One possibility is that the forces between the diffracting planes responsible for these haloes are great and consequently the thermal effects are small. The alternative possibility is that they are due to the interference between the different groups in the molecule.

In the case of tetranitromethane, an investigation has been made by Krishnamurti [1] in solutions. In dilute solutions, the outer halo was observable and this could not be expected if it was due to intermolecular interference. This and the small thermal effect may be taken as evidence that this is possibly the pattern of the molecule.

In the other two liquids, similar investigations in solutions caused the outer halo to be washed off, indicating that they are due to intermolecular interference and hence the small thermal effect is probably due to the enormous crystalline forces.

It is not difficult to see that this is the case, if we take into account the dimensions corresponding to these haloes.

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[1] *Loc. cit.*

The spacings of the outer haloes in ethyl-phthalate and *o*-nitro benzaldehyde, 4·2 and 3·8 A, are smaller than the thickness of the benzene ring. It is well known that the liquids have a benzene ring with long groups attached to the same. The smaller spacing indicates the close packing of the diffracting planes and the forces between these planes may consequently be expected to be great. These are not easily overcome at moderate temperature.

The haloes of a liquid contract differently, the inner ones contracting more quickly than the outer and this brings out the relation between the liquid and the crystal.[1] It is a well known fact that crystals exhibit anisotropy in thermal, electrical, magnetic and other physical properties. In the liquid state the changes in the molecular spacing are also different in different directions. A quantitative discussion of this property requires a thorough investigation of simple crystals in their crystalline form and the liquid at widely different temperatures and is beyond the scope of the present work.

11. *Theory of Scattering by Dissolved Molecules.*

If we consider the dissolved molecules as small spheres of specific inductive capacity K suspended in a medium of specific inductivity K_1 the problem may be treated as that of a small sphere of uniform optical quality according to the method of Lord Rayleigh.[2]

In general, the calculation can be carried out in the optical case only when the circumference of the sphere does not exceed a few wave-lengths. This condition is satisfied in the case of X-rays if the molecules are considered as the diffracting spheres, as for example with a cane sugar or glucose molecule, having a radius of 3·55 and 2·895 A.U. and the diffracting wave-length 1·54 A.U. of copper. But when the relative refractivities are small enough, even this restriction can be dispensed with as has been pointed out by Lord Rayleigh. The formulation of the problem of the optical case is thus strictly applicable for the case under consideration.

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[1] A theory of liquid diffraction has been worked out recently by Kedareswar Banerjee taking the liquid as degenerate crystal. Results under publication.

[2] Scientific papers, Vol. VI, page 518.

Now the expression for the total intensity of scattered radiation, when the incident beam is unpolarised is given by Lord Rayleigh as

$$1/1_0 = \frac{k^4 \mid p^2 \mid}{16\pi^2 r^2}, \text{ where } k = 2\pi/\lambda \quad .. \quad (1)$$

r = the distance between the point at which the intensity is to be estimated and the volume element of scattering.

$$1p^2 1 = (K-1)^2 \, 4^2 \Pi^2 R^6 \frac{(\sin m - m \cos m)^2}{m^6}$$

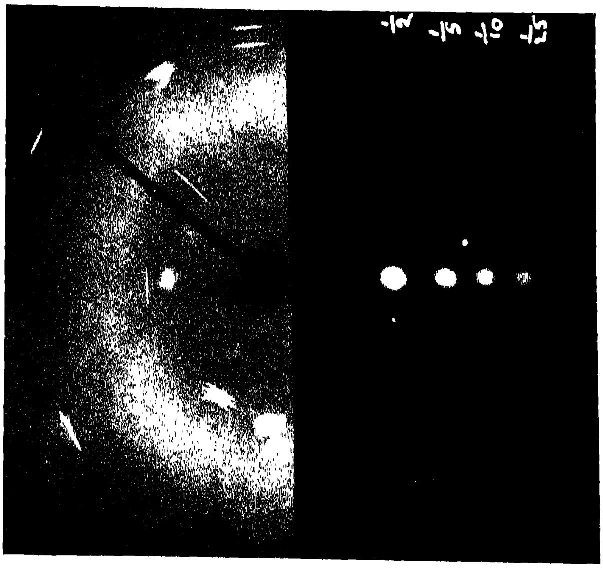
Here K is the specific inductive capacity of the material of the sphere, that of the surrounding medium being unity, R the radius of the diffracting sphere and

$$m = 2k \text{ R } \cos. \chi/2 \text{ and } \chi = \pi$$

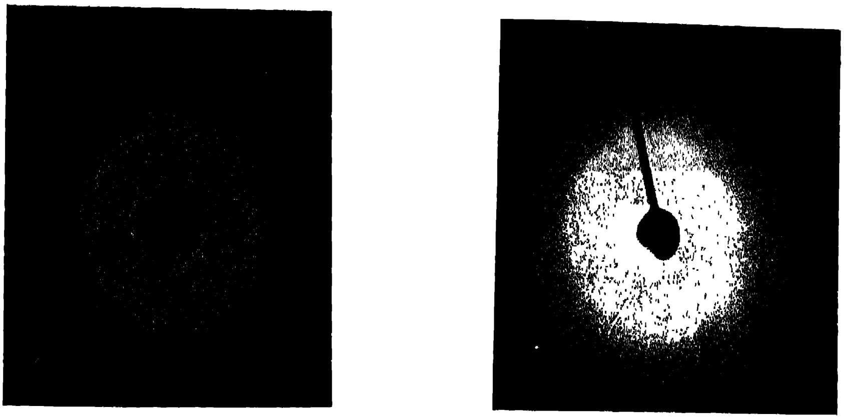
in the forward direction of the primary beam. As mentioned above the restriction that the relative refractivities must be small *i.e.* $(k-1)$ must be small, can be dispensed with, since R is not large when compared with the wave-length in the present problem.

We may thus transform the expression for $\mid p^2 \mid$ into a convenient form

$$\mid p^2 \mid = (K - K_1) 4^2 \pi^2 R^6 \frac{(\text{Sin } m - m \cos m)^2}{m^6} \quad ... \quad (2)$$



Water
Comparison of Primary and Scattered Beams



Cold

Hot

Cyclohexanone

X–Ray Diffraction in Liquids

where k_1 is now the specific inductive capacity of the surrounding medium. When χ is nearly equal to π *i.e.*, in the forward direction

$$\frac{\text{Sin } m - m \cos m}{\quad} = 1$$

and is the maximum value.

Therefore, in approximately forward direction the intensity

$$I/I_0 = \frac{k^4(K-K_1)}{16\pi^2 r^2} \times \frac{4^2\pi^2 R^6}{9} = \frac{16\pi^4 R_6 (K-K_1)}{9\lambda^4 r^2}. \quad \ldots \quad (3)$$

For the high frequencies with which we are dealing in the case of X-rays, the permeability of the medium may be considered as unity and

$$k = \mu^2 \text{ and } \mu = 1 - \frac{n\,e^2}{2\pi\, m\, \nu^2}$$

where n is now the number of electrons per unit volume, the other letters having the usual significance.

After small transformations the expression (3), may be written as

$$I/I_0 = \frac{16\pi^2 R^6 e^4 (n_2 - n_1)^2}{9r^2 m^2 c^4} \quad \ldots \quad (4)$$

for a single diffracting sphere, where n_2 and n_1 are now the number of electrons per unit volume of the dissolved substance and the solvent respectively.

In the case of a dilute solution, if there are N molecules in unit volume and these are distributed at random, the total intensity is N times that given in (4). For, the phases of the waves starting from the solute molecules are uncorrelated and no interference is possible. Thus in the forward direction

$$I/I_0 = \frac{N.\ 16\pi^2 R^6 e^4 (n_2 - n_1)^2}{9r^2 m^2 c^4}. \quad \ldots \quad (5)$$

Expression (5) is perfectly general, the only restriction being the circumference of the sphere should not exceed a few wave-lengths, and the intensity is to be estimated when $\chi=\pi$ (nearly).

We may now apply this to the case of cane sugar dissolved in water in 1:3 concentration by weight. The actual number of molecules in the scattering volume element *i.e.*, in $1\cdot7\times10^{-3}$ c.cs. is equal to $1\cdot1\times10^{18}$ and could be easily calculated from the concentration, r the distance of the plate from the cell is equal to 4·7 cms. n_2 is equal to $5\cdot09\times10^{23}$ and n_1 is equal to $3\cdot369\times10^{23}$.

$$R=3\sqrt{\frac{m}{d}}\Big/2=3\cdot55\text{ A.U.}$$

which is approximately the radius of the cane sugar molecule. Substituting these values in (5), I/I_0 is equal to $4\cdot1\times10^{-6}$ for cane sugar solution. In the case of glucose 1:3 concentration, similar calculation yields I/I_0 to be equal to $2\cdot4\times10^{-6}$. In this case R is equal to 2·895 A.U. and n_2 is equal to $4\cdot98\times10^{23}$. The latter quantity is nearly the same as for cane sugar.

We may now take into account the small inclination of the scattered beam with that of the primary, for it is possible to make the comparison at about 4° only, due to the halation round the central beam. This diminishes the observed intensity according to the variation of the function

$$\left(\frac{\operatorname{Sin} m-m\cos m}{m^3}\right)^2.$$

For copper wave-length and the radius of the cane sugar molecule, actual evaluation shows that at an angle of 12° with the primary beam, the intensity on the photographic plate should be 1/100 of that in the forward direction. At an angle of 4°, the intensity is about 3/4 of that of the maximum.

The respective intensities calculated at 4° are thus 3×10^{-6} and $1{\cdot}8 \times 10^{-6}$ (approx.) for the solutions under consideration. These may be compared with the experimental values $1{\cdot}2 \times 10^{-6}$ and $0{\cdot}8 \times 10^{-6}$.

Qualitatively the increase the scattering at small angles has been observed in solutions by Krishnamurti and Watanabe in a number of cases.

The small experimental value is possibly due to the fact that all the dissolved molecules are not randomly distributed at these concentrations, a small percentage of them still arranging in a regular manner or attaching themselves with water molecules. Complete randomness in distribution may be expected only at very high dilutions. But under such conditions the effect is not observable in the X-ray patterns unless the quantity $(n_2 - n_1)$ is large. In molecules if R is kept moderately large and at the same time they contain also a large number of heavy ions, the conditions are better for the observation of the intensity. But in the case of X-rays a difficulty occurs due to the absorption.

R cannot be increased considerably, since it is restricted by the condition that the circumference should not exceed a few wave-lengths. It is also a disadvantage to reduce R with a view to increase $(n_2 - n_1)$ since I/I_0 varies as R^6. Both conditions are to be suitably adjusted.

It is thus seen that the same considerations as in optics, treating the molecule as a dielectric sphere of uniform optical quality in the X-ray region, lead to results which are fairly satisfactory, and of the same order as obtained in experiments, when the errors in the latter are considered.

It is also interesting in this connection to draw attention to a note in Nature by Prins,[1] who observes an increase in the scattering at small angles in solutions of carbon tetra-chloride in benzene and in aqueous solutions of potassium iodide.

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[1] Prins. " Nature " 123, 84, 1929. After the paper was written, another contribution by Prins on X-ray diffraction has also appeared in Phys. Zeit. *30*, 525 (1929).

My heartfelt thanks are due to Sir C. V. Raman F.R.S., for his kind help and suggestions during the course of the investigation. My thanks are also due to Mr. Manian for the help rendered during these experiments. These were conducted in the Laboratory of the Indian Association for the Cultivation of Science.

X-Ray Study of Vitrains

By

C. Mahadevan.

(Plate XIX)

(*Received for publication, 15th August, 1930.*)

Abstract.

Vitrains of varying proximate composition and of different geological ages [upper palaeozoic and tertiary] were examined by x-ray diffraction methods. All the coals give two halos, one intense and the other comparatively faint. The older coals give spacings of 3. 37A.U. for the inner (intense) and 2.12 A.U. for the outer (faint) halo. The corresponding value for the newer (tertiary) coals are slightly higher, *viz.*. 3·50 A.U. and 2·21 A.U. respectively. In all these patterns, a general scattering between the direct spot and the halos is observed ; the intensity of the general scattering is seen in the case of the older coals to be approximately proportional to the sum of "moisture-content" and "volatile matter" rather than to either of them individually. A departure from this relationship is however observed as we proceed to newer coals. This group differs from the older in that the x-ray patterns of these coals show the same intensity of general scattering for an appreciably smaller amount of "moisture-content" and "volatile matter." Amongst the members themselves of the group of newer coals, correspondence similar to that noted in the case of older group of coals is observed. The above facts, while suggesting a similarity of the coal substance, seem to indicate that coalification has not proceeded to a mature stage in the newer group of coals.

The coals were dehydrated and freed from their "volatile matter" and x-ray patterns of residual products obtained. With dehydration, the general scattering clears to some extent and nearly disappears when the coals are freed from "volatile matter." Such a change is also accompanied by an increase in the width of the halo.

The spacings "a" for the peak intensity of the halo for the residual products in all these cases are however the same as those for the untreated samples. Coals with low 'moisture content' and "volatile matter" have fairly defined edges in the diffraction halo ; with the increase of these two, the halos are seen to show diffuseness of edges.

The sizes of the diffracting particles were calculated to the correct order of magnitude from Laue's formula for representative cases and the values were found to be of colloidal dimensions in all of them.

The "α and β products" of some of the vitrains were studied : they give the same specings as do the untreated coals ; but the width of the halos (as measured between points where the intensity has fallen to half its maximum) are seen to have increased a little and in addition there is seen intense but uniform scattering between the direct spot and the halos ; the intensity of this scattering is greater in the case of "β product" than in that of the "α product." The gamma products give patterns similar to those described in the earlier paper.

From nearly washed out or diffuse patterns obtained for the ash of some of the coals, it is surmised that in vitrains, the mineral matter is present in a colloidal state.

1. *Introduction.*

It is now well established that of the four ingredients[1] constituting banded bituminous coals, vitrain is the nearest approach to the pure coal substance and the other three varieties are more or less heterogeneous in their structure and composition. In two[2] earlier papers on the study of coal problem by X-ray diffraction methods, the author brought out the fundamental difference between the three coals vitrain, durain and fusain. In one of those contributions, the colloidal nature of vitrain and a complex six carbon ring acting as the effective diffracting centre for the patterns obtained were suggested.* In the earlier investigations only a few vitrains of the same geological age were examined. It was thought that a more detailed work on vitrains of different composition and age would help in elucidating several problems in coal study, so far either untouched or just superficially understood. Vitrains from the permocarboniferous to middle tertiary ages were obtained from the Geological Survey of India through the kindness of Dr. L. L. Fermor and Dr. C. S. Fox for the purpose. The author's thanks are due to these gentlemen for the specimens for this study.

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[1] M. C. Stopes. Proc. Roy. Soc., (B) Vol. 90, pp. 470-487, London, 1918.

[2] C. Mahadevan, Ind. Jour. Phys., Vol. IV, pt. 2, pp. 79-98 (1929).
Ind. Jour. Phys., Vol. IV, pt. 6, pp. 457-466 (1930).

2. *X-ray pattern of untreated vitrains.*

Examining table I,* it is seen that the samples investigated constitute a group of coals having varied 'moisture content' from about 1-15% ; the 'volatile matter' ranges from about 25% to 40%. There is no rise in the 'volatile matter' corresponding to a rise in moisture content in the coals. Thus for instance, specimens 6 and 7 have 2·26°/$_0$ and 2·29°/$_0$ of 'moisture content' and 36·42°/$_0$ and 36·49°/$_0$ of 'volatile matter' respectively. In the next case, for a 'moisture content' of 9·61°/$_0$, the 'volatile matter' is 38·20°/$_0$, *i.e.*, for nearly thrice the increase in the previous 'moisture content' the increase in the 'volatile matter' is about one-sixteenth. Although there is no simple relationship between the two it is nevertheless seen that a high 'moisture content' is usually accompanied by high 'volatile matter.'

In column 9 of table I the sum of 'moisture content' and 'volatile matter' for each coal is given. In column 11 of the

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* The figures for the proximate analyses of the vitrains studied (except for numbers 1 & 5) are all taken from Dr. Fermor's paper on 'Density and Composition of Indian vitrains.' (Rec. Geo. Sur. Ind. Vol. LXII, Pt. 2. pp. 189-228, 1929.) The names of the analysts are given in that paper. No. 1 is a Jharia coal analysed with the help of Mr. S. Venkateswaran of Govt. Test House, Alipore. The analyses for No. 5 (Muralidih) is from the presidential address of Dr. C. S. Fox before the Geology section of the Ind. Sc. Congress, Madras, 1929. The analytical values given for Nos. 1 & 5 were on dry basis, and have been recalculated for the original samples taking moisture content also into consideration.

All the coals studied in this paper except No 12 (Skye vitrain) are from Indian empire. The Skye vitrain is from Scotland.

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different composition and age would help in elucidating several problems in coal study, so far either untouched or just superficially understood. Vitrains from the permocarboniferous to middle tertiary ages were obtained from the Geological Survey of India through the kindness of Dr. L. L. Fermor and Dr. C. S. Fox for the purpose. The author's thanks are due to these gentlemen for the specimens for this study.

2. *X-ray pattern of untreated vitrains.*

Examining table I,* it is seen that the samples investigated constitute a group of coals having varied 'moisture content' from about 1-15% ; the 'volatile matter' ranges from about 25% to 40%. There is no rise in the 'volatile matter' corresponding to a rise in moisture content in the coals. Thus for instance, specimens 6 and 7 have 2·26% and 2·29% of 'moisture content' and 36·42% and 36·49% of 'volatile matter' respectively. In the next case, for a 'moisture content' of 9·61%, the 'volatile matter' is 38·20%, *i.e.*, for nearly thrice the increase in the previous 'moisture content' the increase in the 'volatile matter' is about one-sixteenth. Although there is no simple relationship between the two it is nevertheless seen that a high 'moisture content' is usually accompanied by high 'volatile matter.'

In column 9 of table I the sum of 'moisture content' and 'volatile matter' for each coal is given. In column 11 of the same table, an index of general scattering deduced from visual observation of the X-ray patterns of the various coals is noted. A perfectly clear space between the direct spot and the diffraction halo is denoted by 0 and a very intense general scattering in the same interspace by 10. It is seen from the table that there is no relation between the general scattering index and either the 'volatile matter' or the 'moisture content' taken individually ; on the other hand, there appears to be a correspondence of the index when these two are taken together for the samples from 1-10 (Table I).

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* The figures for the proximate analyses of the vitrains studied (except for numbers 1 & 5) are all taken from Dr. Fermor's paper on 'Density and Composition of Indian vitrains.' (Rec. Geo. Sur. Ind. Vol. LXII, Pt. 2. pp. 189-228, 1929.) The names of the analysts are given in that paper. No. 1 is a Jharia coal analysed with the help of Mr. S. Venkateswaran of Govt. Test House, Alipore. The analyses for No. 5 (Muralidih) is from the presidential address of Dr. C. S. Fox before the Geology section of the Ind. Sc. Congress, Madras, 1929. The analytical values given for Nos. 1 & 5 were on dry basis, and have been recalculated for the original samples taking moisture content also into consideration.

All the coals studied in this paper except No 12 (Skye vitrain) are from Indian empire. The Skye vitrain is from Scotland.

Specimens 11 and 12 show an index far too great for their 'volatile matter' or 'moisture content' or their sum ; but between themselves they indicate the same regularity as the other group (1-10) does within its members. Thus two distinct groups in the vitrains studied can be identified, each group showing amongst its members a correspondence between the general scattering and the sum of 'moisture content' and 'volatile matter.' The significance of the existence of two such groups will be discussed in a later section.

A reference to fig. 1 which contains the microphotometer-curves of representative untreated vitrains brings out this point very instructively. A clear space between the direct spot and diffraction halo shows itself as a deep saddle between A the 'direct spot' and B the peak of the halo. With the increase in the general scattering between the direct spot and the halo, the saddle gradually straightens until for patterns showing an intense general scattering, there is almost just a straight curve from A to B, without any sag in between them. Phularitand vitrain (V.M+M.C=28·74%)* shows a deep saddle in evidence of the clear interspace. For Bullari vitrain (V.M+M.C=32·91%) the saddle is not so deep. The Lohpiti specimen (V.M+M.C=38·68%) has a curve somewhat gradual, but the sag is very clear. In the curve for

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* V. M. and M. C. stand for "volatile matter" and "moisture content" respectively.

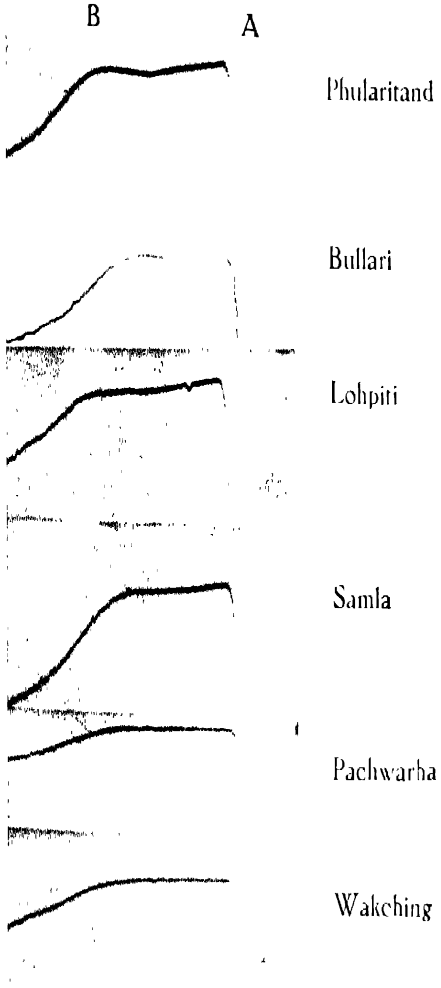

Fig. 1

(Untreated vitrains)

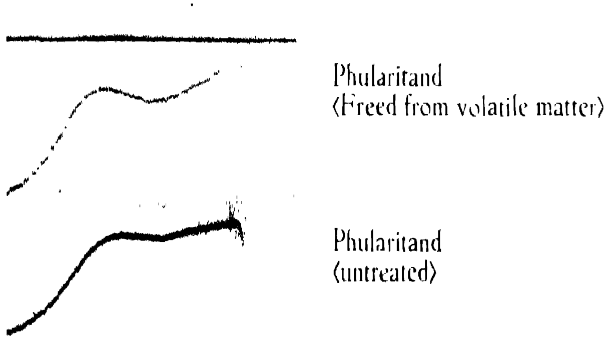

Fig. 2

Samla seam ($V.M+M.C=47{\cdot}81\%$) just a little bend is seen. Pachwarha vitrain ($M.C+V.M=56{\cdot}62\%$) gives quite a straight line. Likewise Wakching vitrain, with M.C. and V.M. totaling to only about 46·63% gives a straight curve much like the Pachwarha vitrain just mentioned above; this last apparent anomaly is the same as the one mentioned before and will be discussed later.

3. *X-ray pattern of dehydrated and volatile matter free coals.*

With a view to understand the part played by "moisture content" in coals, representative specimens, *viz.*, Phularitand, Samle seam, Tch I., Pachwarha, Wakching and Skye vitrains were dehydrated and the X-ray pattern of the residual coals were obtained, (Table II). In all these cases, the diffraction patterns of the dehydrated coals show a little clearing up of the general scattering; *i.e.*, the interspaces between the direct spot and the two halos are in each case comparatively clearer. In addition, a little widening of the halos is easily perceived. (See Table III). For the Phularitand coal the width to which the intensity falls to half the maximum has an increase from 2·3 to 2·4 mm. The Samla seam vitrain now shows an increase from 3·1 to 3·4 mm. For Pachwarha, Wakching and Skye vitrains the increase is 5, 3 and 3 mm. respectively. It is interesting to note that even in the untreated state, the width of the halo increases gradually with the increase in 'moisture content.' The size of the diffracting particle was in each case calculated from Laue's recently deduced formula[3]

$$B=\frac{\frac{\pi}{2}\frac{\omega}{n}\left(\frac{r}{R}\cos^2\frac{2}{\theta_h}\right)^2}{\sqrt{1+\left(\frac{\omega r}{nR}\cos^2\frac{\theta^h}{2}\right)-}}$$

where $\omega=\frac{1}{1{\cdot}8}=0{\cdot}55$

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[3] Laue, Von. Zeits. Krist. Vol. LXIV, p. 115 (1926).

B=the angular breadth of the halo measured between points where the intensity has fallen to half its maximum,

θ=the angle of diffraction,

r=the radius of the cylindrical preparation,

R=Radius of the camera,

and $n=\dfrac{\lambda}{4\pi\, mai}$ where *mai* is the magnitude which is to be calculated.

The above formula suitably modified to our case (due to difference in camera model) was thus simplified :—

$$\frac{1}{d}=\frac{1{\cdot}1}{\lambda}\left[\mathrm{B}\cos\theta/2-\frac{1}{\mathrm{B}},\frac{\pi^2t^2}{4\mathrm{R}^2}\cos^3\frac{\theta}{2}\right]$$

where t is the thickness of the flake of substance,
R is the distance of the camera from the substance,
d is the linear dimension of the particle as measured perpendicular to the plane of reflection,
and B is the angular width of halo less the natural angular width due to dimensions of apparatus.

It has to be pointed out here that the values obtained for the size of the particles may not be taken as absolute ; none the less, it may be expected that the relative orders of magnitude are correctly deduced from these calculations.

The ‘ volatile matter ’ of some of the representative coals was driven out and the residue in each case studied ; in all of these, it is found that the general scattering has disappeared completely ; in addition, the halos have all broadened perceptibly ; they are seen to be even broader than the halos obtained for the dehydrated coals.

The intensity maxima in all these cases are unaltered. Another very interesting feature associated with the X-ray pattern of coals freed from “ volatile matter ” requires to be emphasised. The patterns from residues of coals in which the ‘ moisture-content ’ and ‘ volatile matter ’ were initially low show rather well defined edges for the halo ; on the other hand, the halos of such residual (freed from " volatile matter ") coal with original high " moisture content " and " volatile matter, " show quite diffuse edges indicating very much smaller particles of diffraction than in previous case. In plate XIX, fig. 2 shows the microphotometer curves of the X-ray patterns of an untreated coal and the residual coal after freeing the same coal of its " volatile matter. " The clearing up of the space between the direct spot and the halos is indicated by a great sagging of the curve.

4. *X-ray patterns of "α, β and γ products " and of ash.*

Some of the coals were extracted with pyridine and benzene and " α, β and γ products " so obtained were studied by the X-ray diffraction methods. From a reference to table IV, it is seen that the spacings " a " for the α and β products are in all cases unaltered ; but the width of the halo * has increased appreciably in the two cases. Besides, there is a very intense and uniform general scattering observed between the direct spot and the inner halo in the case of the β product. The scattering is not so intense in the case of α products. As observed in the earlier paper [4] the gamma compounds give two intense halos and a faint one with about the same spacings described therein.

To study the ash patterns of these vitrains, three of the coals were ignited in a platinum crucible till constancy of weight was ensured. The ash thus obtained was studied. They all give three nearly washed out rings in evidenc of the fine colloidal state in which the mineral matter is present. For the Lohpiti vitrain, the halos are somewhat distinct.

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* By " width of the halo " is meant the distance between two points on the halo where the intensity fades to half its maximum.

[4] C. Mahadevan, Ind. Jour. Phys., Vol. IV, Pt. 2, *loc. cit*

5. *Discussion.*

(*a*) *Geological age and X-ray patterns.*

It is now widely recognised that the process of coalification from peat deposits is a function of time and the gradual pressure of the overlying sediment. When this process is in nature interfered with by heat from igneous intrusions, it is well-known that the coal beds in contact are adversely affected and become almost useless as commercial products. The true bituminous coals may be considered as " no mere residue but an organically rewrought 'condensed' material—largely a synthetic artifact."[5] It is obvious that in the process of such metamorphosis the part played by time is of great significance. In view of this, various attempts have been made to study the constitution of coal with special reference to their age.

In this connection, it is relevant to refer to a recent work of Fermor,[6] who from an examination of the 'proximate analyses' of coals of different geological ages is unable to deduce any relationship between the geological age and 'moisture content' or 'volatile matter'; there is a tendency for the older vitrains to show lower 'volatiles' and higher 'carbon'. It is significant, however, that in the same stratigraphical horizon he finds diminution of the moisture content with increasing depth. One of his suggestions for this peculiarity is highly interesting. A fundamental difference in the original vegetable matter may be presumed to be responsible for the anomaly observed between the older and newer coals; *i. e.*, given vegetable matter of identical nature to start with, one could expect to find change in proximate composition with progressive age. The significance of such an explanation to account for the difference in the composition as determined " by proximate analyses " can hardly be minimised. None the less, it must be pointed out that this method of breaking up coal is more or less artificial and does not represent the nature of either the chemical complexes of the fundamental coal substance or of the associated constituents. From a study of a more rational method of decomposition of coal, Fischer, Broche and Strauch suggest that with increasing geological age of the coals the ratio of free hydrocarbons to resins increases whilst the decomposition temperatures of the resins are raised.[7]

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[5] H. E. Armstrong, Proc. Roy. Soc. (A), Vol. 127, p. 270 (1930).

[6] L. L. Fermor, Rec. Geo. Sur. Ind., Vol. LXII, Pt. 2, pp. 212-216 (1929).

The X-ray study on the other hand offers another powerful means in the attack of the problem of the effect of age on coals. The apparent anomaly between the results of the Gondwana (upper palaeozoic) group of vitrains and the tertiary coals was pointed out in section 2. It was seen that the spacing " *a* " for the Gondwana vitrains, inspite of the variable compostion shows a constancy of 3·38 A. U. for the inner and 2·12 A. U. for the outer halo corresponding to finely divided graphitic carbon spacings. The two tertiary coals differ from the above group in two essential points. The corresponding figures for the spacings are =3·5 A.U. and 2·2 A.U. respectively and are thus slightly higher. The scattering index gave values higher than those obtained for the corresponding Gondwana coals. Such results are intimately connected with the geological age of the two groups and will be examined here in greater detail. The general similarity of the patterns of the tertiary and Gondwana (permocarboniferous) coals suggests a great similarity of the fundamental coal substance.* On the other hand, the slight but definite increase in the corresponding spacings of tertiary coals points to a structural difference. The importance of the structural factor in the spacings obtained for the peats and coals was pointed out elsewhere.[8] The tertiary coals occupy presumably an intermediate place between peaty lignites and (mature) bituminous coals.

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* It is interesting to note that very recent work of Prof. Bone and his collaborators (Proc. Roy. Soc., Vol. 127, p. 493, 1930) supports such an inference.

[7] Fischer, Broche and Strauch, Brennstoff-Chem., 1924, Vol. V, p. 299 and 1925, Vol. VI, p. 33.

[8] Ind. Jour. Phys., Vol. IV, Pt. VI, p. 461 (1930).

Two coals of different geological ages and of comparable "proximate composition" give the following results: the older coal with appreciably a greater 'moisture' content and 'volatile matter' shows just about the same general scattering as a more recent coal of less 'moisture content' and 'volatile matter'. This is clearly shown in the microphotometer curves in fig. 1. Coals of the same age show a progressive correspondence amongst themselves. The apparent anomaly is observed only when we proceed to a newer coal. The reason for this is understood if we remember that coalification has not reached a mature stage in the newer coals and there are still present appreciably greater material giving rise proportionally to greater general scattering. With the increase in age, the constituents condense and reach greater stabilisation. This shows itself in the diffraction pattern indicating a constancy of the spacing "*a*" for the intensity maxima of 3·37 A.U. and 2·12 A.U. respectively for the inner and outer halos and a correspondingly less general scattering than the patterns for newer coals.

Thus it is seen, that coals of the same geological age show correspondence between their "proximate composition" and X-ray pattern, but the newer coals with apparently the same "proximate composition" as older coals reveal a looser structural state in keeping with their age.

(*b*) *Moisture content and volatile matter.*

The colloidal nature of the coal substance particle and the complexity of association of water in coals has been thoroughly discussed by Mack and Hulett.[9] They have indicated that 'moisture content' as deduced from dehydration under low pressure at room temperature with a suitable agency as P_2O_5 may not be identically from the same source as the 'moisture content' obtained by heating for some hours at 105°C. In the second case there is bound to be some chemical reactions of which a little of the water calculated as 'moisture content' may be the part. Besides, all the water in intimate colloidal association with the coal may not be driven out by these methods. Without going into a detailed examination of the vast amount of literature on moisture and water in coals, we may mention that it is well recognised that the 'moisture content' of a coal as determined by dehydrating at 105°C does not indicate the total amount of water present in the coal and that some little part of the moisture so determined may have been formed chemically in the process of thermal decomposition. At the same time, it may be assumed that the 'moisture content' of the coal gives a very nearly accurate *relative idea* of the amount of water in the coal.

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[9] E. Mack and G.A.H. Hulett. The water content of coal; with some ideas on the Genesis and Nature of coal. Am. Jour. Sc., Vol. XLIII, 4th series, No. 254, pp. 89-110 (1917).

Also see Campbell, Jour. Soc. Chem. Ind., Vol. XXXII, No. 2 (1913).

The correspondence of the general scattering index to the sum of 'moisture content' and 'volatile matter' and not to either of them individually seems strongly to suggest that these two are more intimately connected than we seem to understand from our existing chemical knowledge about the constitution of coals and that the process of breaking them in the 'proximate analyses' does not divide the two uniquely.[10] It is intended to study this problem in greater detail. The presence of water as a phase in the colloidal system of coals has long been recognised. Reference was made in an earlier paper to Fermor's conclusions from a study of the density-moisture content relationship of vitrains.[11] Fermor's subsequent work [12] on "the Density and Composition of Indian vitrains" confirms his previous conclusions with regard to this point.

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[10] W. T. Thom, Jr. "Moisture as a component of volatile matter," Colliery Guardian, Vol. 130, p. 568 (1925).

[11] L. L. Fermor, Rec. Geo. Sur. Ind., Vol. LX, Pt. 2, p. 348 (1928).

[12] L. L Fermor, Rec. Geo. Sur. Ind., Vol. LXII, Pt. 2, p. 220 (1929).

In the patterns for the dehydrated vitrains, the partial clearing up of the X-ray pattern and the increase in the width of the halo are extremely significant. The first fact shows that the 'moisture content' to some extent is responsible for the general scattering. In addition the broadening of the halo points to the decrease in the size of the diffracting particle ; in other words, some of this 'moisture content' was in intimate association with the coal substance in the untreated state and as soon as some of the water is driven off, the particle naturally gets smaller. With the driving away of volatile matter, it appears that precisely the above phenomena are carried to completion. Hence, the general scattering has all vanished and the interspaces between the direct spot and halos are nearly clear ; the width of the halo has increased perceptibly. But in all these cases the spacing '*a*' of the halos are constant. From these results, it is evident that the 'moisture content' and 'volatile matter' were in intimate association with the residual carbonaceous matter and that both together were responsible for the general scattering. The form in which they existed in combination with the residual carbon is not however indicated. The persistency of the value of the spacings "*a*" in all these cases suggests strongly a structural stability of the diffracting particle in spite of other compositional differences ; the dimensions obtained for these spacings are those for the benzene or six carbon (graphitic) ring and may be surmised to be the nuclei for the mature fundamental coal substance and associated hydrocarbons. A detailed investigation is in progress on these problems.

It has finally to be mentioned that from a study of a number of vitrains, only the most obvious conclusions have been indicated warranted by the results. Discussion of these results in relation to the existing theories in the coal problem is reserved for a later publication.

6. *Experimental.*

A Shearer tube of the usual type with a aluminium cathode and copper target was used as the source of X-rays. The initial vacuum in the tube was obtained by Cenco hyvac and the finer vacuum by two Waran's mercury diffusion pumps. The high tension was supplied by an oil cooled transformer with an alternate spark-gap of 3·5″. Alternating current at 160 volts was supplied to the primary from a rotary converter. The current in the secondary circuit was from 5 to 6 milliamps. The time of exposure varied from 3 to 8 hours according to the substance.

For dehydration, the coals were finely powdered and heated in air oven at 105° till no loss of weight was observed at successive weighings in an interval of half an hour. The driving out of the volatile matter was likewise done by the standard method—by heating at 950°C the powdered coal in a closed platinum crucible for 7 minutes with a flame enveloping the crucible.

The breaking up of the coal into α, β, and γ compounds was accomplished by the method described in the earlier paper, *viz.*, in an all-glass soxhlet's apparatus, the extraction of the coals being carried out with moisture free and "extra pure" Khalbaum's pyridine and benzene. The ash from the coals was obtained by igniting in a platinum crucible the coal with a mecker burner till all the carbonaceous matter was driven out and constancy of weight was assured.

The same X-ray camera described in the previous experiments was used. After obtaining the diffraction angle of the halos the spacing "a" was calculated from the Bragg Formula

$$a = \frac{\lambda}{2 \sin \theta/2}$$

The size of the diffracting particle was obtained from Laue's formula, suitably modified for the different type of camera used in these experiments. The dehydrated, volatile matter free and extracted coals were held in a mica-cell container as they lost the property of coherence with these treatments.

The experiments were carried out in the laboratories of the Indian Association for the Cultivation of Science. The author's most grateful thanks are due to Sir C. V. Raman, Kt., F.R.S., for his continued interest and guidance in the problem.

TABLE I.

Untreated Coals.

	Coal.	Register of field number.	Age.	Moisture content.	Volatile matter.	Fixed carbon.	Ash.	Moisture + volatile.	Description of X-ray pattern.	Intensity of scattering Index.	$a_1 = \frac{\lambda}{2 \sin \theta_1/2}$	$a_2 = \frac{\lambda}{2 \sin \theta_2/2}$	
1	2	3	4	5	6	7	8	9	10	11	12	13	
											A.U.	A.U.	
1	Jharia		Jharia Barakar	0·79	22·60	62·82	13·8	23·39	A little central scattering Interspaces very clean.	4	3·37	2·11	Upper Palaeozoic.
2	Phularitand	Fx	Jharia Barakar	0·85	27·89	70·90	0·36	28·74	A little central scattering Interspace clear.	5 −	3·37	2·13	
3	Bullari		Jharia Barakar	1·67	31·24	63·12	3·97	32·91	Interspace fairly clear.	5 +	3·37	2·13	
4	Bokaro Seam 13 Joint Colliery	F 377	Bokaro Barakar	1·99	27·47	68·23	2·31	29·46	Central scattering Interspace clear.	5	3·38	2·12	
5	Muralidih		Jharia Raniganj	2·20	28·67	55·77	12·9	30·87	Interspace clear.	5	3·37	2·12	
6	Lobpiti	Fx	Jharia Raniganj	2·26	36·42	56·57	4·75	38·68	No pronounced central scattering. Interspace not very clear.	6 +	3·39	2·13	
7	Barangua	Fx	Jharia Raniganj	2·29	36·49	57·62	3·60	38·78	A little central scattering. Interspace as above.	6 +	3·38	2·13	
8	Samla	Rr_4	Raniganj Raniganj	9·61	38·20	51·79	0·40	47·81	No central scattering, Interepace showing good general scattering.	8	3·38	2·13	
9	Talcher Handidhua	Tch_1	Talcher Barakar	15·08	38·59	45·76	0·57	53·67	No central scattering. Interspatial scattering intense.	9	3·37	2·12	
10	Pachwarha Amrapara	Rj_2	Pachwarha Barakar	16·26	40·36	41·27	2·11	56·62	Very intense general scattering.	9 +	3·38	2·12	
11	Wakching	Fx	Nazira Tertiary	8·15	38·48	52·98	0·89	46·63	Very intense interspacial general scattering.	9 +	3·49	2·21	Tertiary.
12	Skye (Scotland)		Scotland Tertiary	11·41	35·85	48·37	4·21	42·26	Very intense general scattering.	9 +	3·51	2·22	

− indicates a little less than. + indicates a little more than.

TABLE II.

Dehydrated and volatile matter free coals.

	Dehydrated.					Volatile matter free.				
Coal.	θ_1	θ_2	a_1 A. U.	a_2 A. U.	Description.	θ_1	θ_2	a_1 A. U.	a_2 A. U.	Description.
Phularitand.	26°22′	42°36′	3·38	2·12	A little clearing of general scattering.	26°22′	42°36′	3·38	2·12	No general scattering Edges fairly sharp.
Lohpiti.						26°22	42°34′	3·38	2·13	No general scattering edges fairly clear.
Samla.	26°23′	42°30′	3·37	2·13	A little clearing of general scattering.	26°23′	42°35′	3·37	2·12	No general scattering outer edge of halo rather diffuse.
Talcher Tch$_1$	26°23′	42°36′	3·37	3·12	,,					
Pachwarha.	26°22′	42°32′	3·38	2·12	,,	26°23′	42°36′	3·37	2·12	No general scattering outer edge of halo very diffuse.
Wakching.	25°28′	40°52′	3·49	2·21	,,	25°27′	42°52′	3·40	2·21	Ditto.
Skye.	25°19′	40°44′	3·51	2·22	,,	25°20′	40°54′	3·51	2·22	Ditto.

TABLE III.

Relative size of diffracting particles.

No.	Coal.	Untreated.		Dehydrated.		Volatile matter free.	
		Width of halo observed in m. m.	Particle size calculated in A. U.	Width of halo observed.	Particle size calculated in A. U.	Width of halo observed.	Particle size calculated in A. U.
1	Phularitand.	2·3	63	2·4	52	2·5	44
2	Lohpiti.	2·6	38			2·8	22
3	Samla seam.	3·1	24	3·4	20	4·8	11
4	Talchir Tch 1	3·3	21	4·1	14		
5	Pachwarha.	3·6	18	4·1	14	5·2	10
6	Wakching.	3·7	17	4·0	15		
7	Skye.	4·0	15	4·3	13	4·9	11

For coals from 1-5, the diffracting angle has been taken as 26°24 (See table II).

For coal 6 (wakching). $\theta = 25°28$ and for 7 (skye) $\theta = 25°20$.

TABLE IV.

Alpha and Beta compounds.

		Alpha product.			Beta product.		
No.	Coal.	a_1	a_2	Description.	a_1	a_2	Description.
1	Bokaro.	3·38	2·14	Intense general scattering.	3·38	2·13	Wider halo very intense general scattering.
2	Phularitand.	3·37	2·13	..	3·37	2·14	,,
3	Lohpiti.	3·38	2·14	,,	3·38	2·14	,,
4	Wakching.	3·49	2·22	,,	3·49	2·21	,,
5	Skye.	3·49	Very diffuse.	,,	Not enough obtained for study.		—

Studies in X-Ray Diffraction: Part III.

Some Aromatic Hydrocarbons in the Solid and Liquid states

By

P. Krishnamurti

(*Plate XX*)

(*Received for publication, 15th November, 1929*)

1. *Introduction.*

During the past few years, the study of the X-ray diffraction haloes exhibited by liquids has received a great deal of attention. It is abundantly clear that these diffraction patterns are determined by the arrangement of the molecules as determined by the physical state of the liquid and the structure of the individual molecules including particularly their size, shape and their electric polarity. The exact nature of the molecular arrangement in liquids, particularly in those cases where the shape of the molecule widely departs from spherical symmetry is not yet fully cleared up. It is obvious that in a dense fluid, the molecules cannot possess the same freedom of translatory movement and rotation as in a gas. Exactly to what extent is this restriction of freedom carried in a liquid ? At one extreme end is the view that the molecules in a liquid are free individual units as in the vapour, and that there is no restriction on their translatory and rotary movements except such as results from the frequent collisions with their neighbours, and the high intrinsic pressures in the fluid. At the other extreme is the view that the molecules tend to form orientated or parallel groups in which the individual freedom has practically disappeared. To the latter view the objection may be raised that the state contemplated would be that of the liquid crystal which, as is well known, is a turbid medium showing birefringence rather than that of a transparent isotropic fluid. In this connection, the theoretical investigations of C. W. Oseen on liquid crystals* are of great interest as indicating that the physical state of a liquid is sharply differentiated from that of a liquid crystal, and that in a true liquid the orientations of a molecule are approximately random in character. It seems reasonable to assume, however, that in an ordinary liquid, the orientative influence of one molecule on another is felt appreciably by its immediate neighbours, so that the complete randomness of the neighbouring molecules with reference to a particular molecule is not possible. Only at a sufficiently large distance (compared to molecular dimensions) from any molecule it is possible to find other molecules oriented at random to that particular molecule. Since we are usually examining sufficiently thick layers of liquids, and since the wavelength of light is large when compared with molecular dimensions, we do not find the characteristic properties of liquid crystals.

The next point is to investigate what exactly is the amount of randomness which one molecule can take up with reference to its neighbours. This is determined to a great extent by the following factors (1) the geometric shape of the molecule, (2) the electric polarity and the positions of the polar groups in the molecule, (3) rotation of the molecule round any axis or vibration about a mean position, (4) thermal agitation by which the distance at which another molecule is quite randomly oriented is made smaller. Let us now consider how these factors influence the X-ray diffraction patterns in the case of long-chain aliphatic compounds and in the case of a flat molecule like hexamethyl benzene. The long-chain hydrocarbons show only one ring, spacing 4·8A which is independent of the length of the chain after a certain length. Since the molecules are non-polar, the geometric form is the main factor influencing the arrangement of the molecules. An approximate parallelism of the molecules adjacent to any molecule is indicated, but due to factors (3) and (4) shown above, they depart to varying extents from an exactly parallel arrangement as that found in the crystal, with the result that a broad ring with a larger spacing than in the solid is obtained. In the fatty acids, in addition to this side by side arrangement, similar arrangement lengthwise is also possible owing to the polar groups coming close together, but it will be seen that any irregularity in the side spacing will affect this considerably, and hence we get an additional faint, broad spacing in the liquid fatty acids. One consequence of the above hypothesis will be that the liquid haloes should get appreciably sharper with increasing length of the chain, and quantitative experiments should be made to detect such a variation.

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* C. W. Oseen, Forts. d. Chemie, Band 20, Heft 2, 1929.

We can next come to consider the case of a distinctly flat molecule like hexamethyl benzene. X-ray examination of the crystal shows that in the molecule all the carbon atoms lie in the same plane, and all the molecules are arranged together in parallel sheets as in graphite. The liquid pattern has been recently examined by the author, and the results set forth in a previous paper.[32] Since the molecule is non-polar, the geometric shape, molecular rotation and vibration and thermal agitation are the factors which determine the X-ray pattern. An arrangement approximately parallel to the discs but departing therefrom to some extent by the other two factors is indicated, and the positions and intensities of the two rings in the liquid pattern are in essential agreement with these views.

In general, a highly anisotropic shape of the molecule is indicated in the X-ray pattern by a very broad ring, but in some cases a somewhat clear region is noticed which divides this ring into two separate rings. By studying a large number of such cases, the present author has come to the conclusion that ortho or meta substitution or both should be present in the benzene nucleus in order to show the separation into two rings, a simple para substitution showing a single broad pattern similar to that of the mono-substituted derivative. Since this is shown by non-polar compounds as well as by polar ones, this should result either from the geometric shape or from the restricted freedom to rotation or oscillation in certain directions brought about by substitution.

The present investigation was started with a view to understand the liquid diffraction phenomena more thoroughly by examining non-polar aromatic hydrocarbons whose crystal structure has been partially or fully analysed, and of whose molecular dimensions we have some clue. The substances include naphthalene and acenaphthene (crystal structure examined by Bragg) and diphenyl, fluorene, phenanthrene, dibenzyl and stilbene (crystals examined by Hengstenberg and Mark).

2. *Experimental Procedure.*

A detachable Shearer X-ray tube was used in these investigations. It was provided with a copper target and a thin aluminium window through which the X-rays could pass without excessive absorption. The tube was worked by a transformer at about 50 K.V. and a fairly steady current of 5-6 milliamperes could be easily maintained in the tube. The radiation emitted consisted of the Kα and Kβ of copper, but since the latter was of feeble intensity, the use of a filter was not considered necessary.

The present work was carried out using a camera provided with an arrangement for maintaining a high temperature. A pyrex tube with openings for entrance and exit of X-rays was surrounded by a coil of nichrome wire and heated electrically. The temperatures attained with different current strengths were obtained, so that the substance could be raised to a temperature just above its melting point. Very thin Jena glass tubes about 1 mm. in diameter were used as containers for the crystalline powder which were introduced into the bigger pyrex tube. The powder pattern was first taken, the temperature raised till the substance melted, and the liquid pattern obtained under the same conditions as the former. The distance between the substance and the plate in this camera was found to be 4·03 cms.

The diameter of the rings, and the extent of the corona, if any, were all measured visually, and the spacings calculated from the Bragg formula

$$d=\frac{\lambda}{2\,\mathrm{Sin}\,\frac{\theta}{2}}$$

3. *Acenaphthene* ($C_{12}H_{10}$) *and Naphthalene* ($C_{10}H_8$).

These two hydrocarbons have been studied in detail by Bragg* and the latter recently by Banerjee.† The data are given below :

Acenaphthene	Naphthalene
Ortho-rhombic	Monoclinic prismatic
$a=8{\cdot}32$	$a=8{\cdot}34$
$b=14{\cdot}15$	$b=6{\cdot}05$
$c=7{\cdot}26$	$c=8{\cdot}69$
$Z=4$	$\beta=122^\circ 49'$
	$Z=2$

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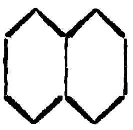
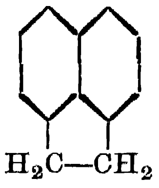
* Bragg, Proc. Phys. Soc., *34*, 33 (1921).

† Banerjee, Ind. J. Phys., *4*, 557 (1930).

Acenaphthene can be derived from naphthalene by substituting two CH_2 groups in the 1, 8 positions.



Naphthalene



Acenaphthene

The unit cell contains four molecules which are situated at the corners and at the centres of all the faces. The molecules at the corners are situated with their lengths parallel to the 110 plane, but those at the centres of the faces point the opposite way. The minimum distance separating two molecules which is evidently the thickness of the molecule is $\frac{c}{2}$ or 3·63 A. The length of the molecule is 8·23 A, slightly smaller than that of naphthalene.

The liquid pattern consists of two well-defined rings, spacings 6·50 A and 3·93 A respectively, the former being the stronger of the two. The pattern is very similar to that given by liquid hexamethyl benzene. The spacing of the outer ring corresponds very nearly to the thickness of the molecule as found in the crystal. Taking the density of acenaphthene (liquid) to be 1·03, the cross-section of each molecule will be

$$\frac{180\times1\cdot66}{1\cdot03}\times\frac{1}{8\cdot23}=25\cdot5A^2.$$

Taking the thickness of the molecule as 3·93A, we get for the breadth 6·48A in very good agreement with the spacing of the first ring in acenaphthene liquid pattern. The strong scattering inside this ring is probably produced by uncertainty in the length spacing of the molecules. Acenaphthene could be regarded as an ortho and meta substituted benzene derivative and hence the presence of two separate rings is observed as in other cases.[20]

Naphthalene.—Bragg supposes that the molecule lies with its length along the *c*-axis, and with its plane along *ab*. But recent measurements of Banerjee indicate that the length of the molecule is slightly tilted from the *c*-axis, and also that the plane of the molecule lies nearer *bc*. We can also see from the model that one molecule cannot approach another closer than $\frac{a \sin \beta}{2}=3{\cdot}53$A. The length of the molecule according to Bragg is 8·34A and its breadth nearly 6A.

The liquid pattern was characterised by (1) a large amount of scattering at small angles to the primary beam extending up to the first ring, (2) a broad halo with a spacing of 5·55A, which was more diffuse at the outer edge, (3) a faint and diffuse maximum at a larger angle (spacing 3·88A). There was large scattering between the first and second haloes, so that their separation was only just visible. The spacing 3·88A is very near the value obtained for the thickness of the molecule in the crystal, while the larger spacing corresponds to the breadth spacing, the strong scattering at small angles showing that no periodicities in the direction of the length of the molecule exist. The liquid pattern shows a great resemblance to that of *o*-xylene where the spacings of the two rings are 5·5A and 3·7A respectively. This is just what it should be, since naphthalene could be considered in a way as an ortho disubstituted benzene derivative.

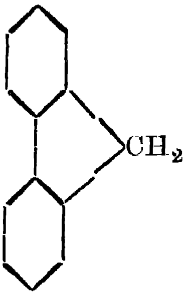
The spacings in the powder and liquid patterns of acenaphthene and naphthalene are given below :

TABLE I

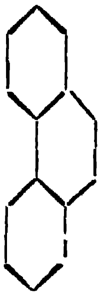
Substance.	Powder.		Liquid.		
	λ in A.	Intensity.	θ in degs.	λ in A.	Intensity.
Acenaphthene	7·21	Strong	13·6	6·50	V. strong
	5·10	,,	22·6	3·93	Strong
	3·49	,,	...	...	...
Naphthalene	7·29	Strong	...	...	...
	4·58	V. strong	15·9	5·55	Strong
	3·44	Strong	22·9	3·88	Med. str.
	3·03	Med. str.	...	...	...

4. *Fluorene* ($C_{13}H_{10}$) *and Phenanthrene* ($C_{14}H_{10}$).

These two substances are usually represented as follows



Fluorene



Phenanthrene

They belong to the monoclinic prismatic class, and the dimensions of the unit cells have been given as follows :—*

Fluorene.	Phenanthrene
$a=8\cdot48$	$a=8\cdot60$
$b=5\cdot73$	$b=6\cdot11$
$c=19\cdot24$	$c=19\cdot24$
$\beta=101^\circ\ 53'$	$\beta=98\ \ 15'$
$Z=4$	$Z=4$

Since the doubling of the molecules per cell in case of fluorene and phenanthrene is followed by a similar increase in the length of the c-axis, as compared to diphenyl the molecules should lie with their lengths along the c-axis. Hence the lattices of fluorene and phenanthrene are composed of double molecules lying end to end. The planes of the molecules may lie along the b-axis, or slightly tilted from it as in the case of naphthalene. Hence, the thickness of the molecules will be approximately $\frac{a \operatorname{Sin} \beta}{2}$, and are $4\cdot15$ A, and $4\cdot26$ A respectively in the two cases.

The spacings of the powder patterns and of the corresponding liquid patterns are recorded in Table II. Only the prominent powder spacings are given, and no attempt is made at great accuracy.

---

* Hengstenberg and Mark, Z. Krist., *70*, 283 (1929).

Table II.

	Powder.		Liquid.		
Substance	Spacing in A	Intensity	θ in degs.	Spacing in A	Intensity
Fluorene	9. 30	Med. Str.	10.2	8.66	Strong
	4. 57	Strong	18.2	4.87	,,
	3. 34	Med. Str.	—	(3. 7)	Limit of general Scattering
Phenanthrene	9. 64	Strong	10.9	8.12	
	4. 88	,,	19.8	4.48	Strong
	4. 00	Med. Str.	—	(3. 6)	,, Limit of general Scattering
	3. 37	Strong			

Fluorene.— The pattern for this substance in the liquid state is characterised by an intense general scattering extending up to about 24°, and the two maxima which could be just made out in this dense background are very diffuse. The first ring has a spacing of 8·66 A while the second has a spacing of 4·87 A. There is a strong scattering within the first ring, and since the latter is also of small size, the presence of any maximum at still smaller angles could not be detected.

In the crystal, the length of the molecule also lies along the *c*-axis, but the latter is long enough to include two molecules end to end. The thickness of the molecule is almost the same as in diphenyl, and the breadth is also the same. But the intersting fact still remains that the pattern for liquid diphenyl is entirely different from that of liquid fluorene, in spite of the essential similarity of crystalline structure and dimensions of the molecules. It appears probable that by the closing up of the two ortho positions to the bond conneecting the two benzene rings through a CH_2 group, the molecule has become flatter in structure than in diphenyl and free rotation about the *c*-axis is rendered more improbable.

Phenanthrene.— The pattern for the liquid shows a remarkable resemblance to that of fluorene considered above. The general scattering extends up to 3·6 A. The two maxima are just visible but are broad and very diffuse. They have the spacings 8·12 A and 4·48 A respectively. As mentioned in the case of fluorene, there is considerable scattering inside the first ring, but it is difficult to detect the presence of any maximum at such small angles.

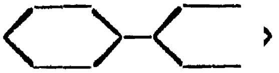
The two spacings for liquid phenanthrene are slightly smaller than those for fluorene. The outer spacing roughly corresponds to the thickness of the molecule in the crystal (4·26 A). This is probably because the molecule now possesses a pronounced flat structure. The length of the molecule in the crystal is 9.6 A and its breadth is 6·1 A, so that an average of these two dimensions may account for the presence of the prominent liquid halo at 8.12 A. A rough calculation of the density can accordingly be made :—

$$\text{Density} = \frac{178 \times 1.66}{(8.12)^2 \times 4.48} = 1.00$$

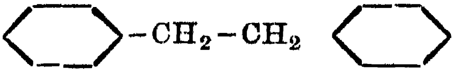
which agrees with the actual value of 1.06/100° C.

5. *Diphenyl* ($C_{12}H_{10}$), *Dibenzyl* ($C_{14}H_{14}$) *and Stilbene* ($C_{14}H_{12}$).

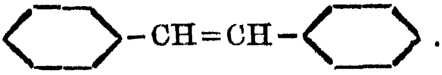
The molecules of these substances are usually represented as follows :



Diphenyl



Dibenzyl



Stilbene

Powder Liquid

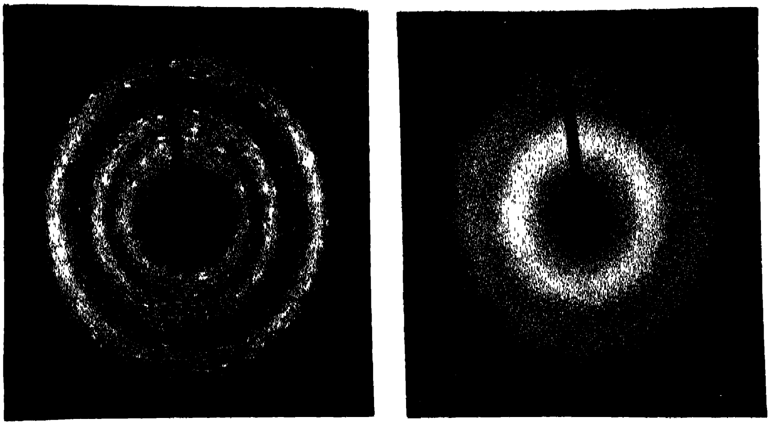


Fig.

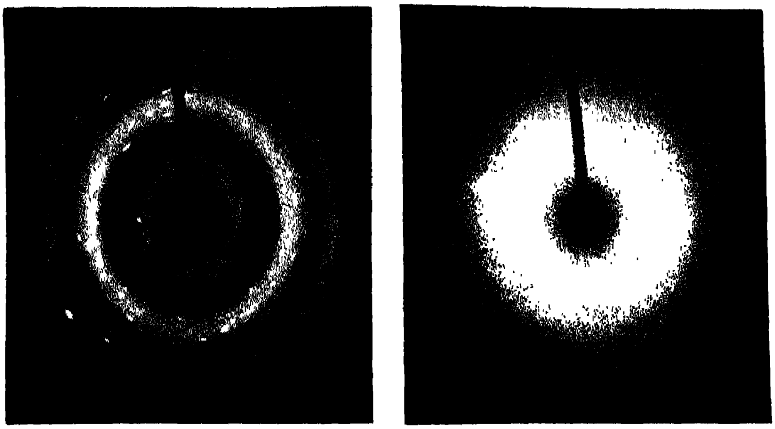


Fig. 2.

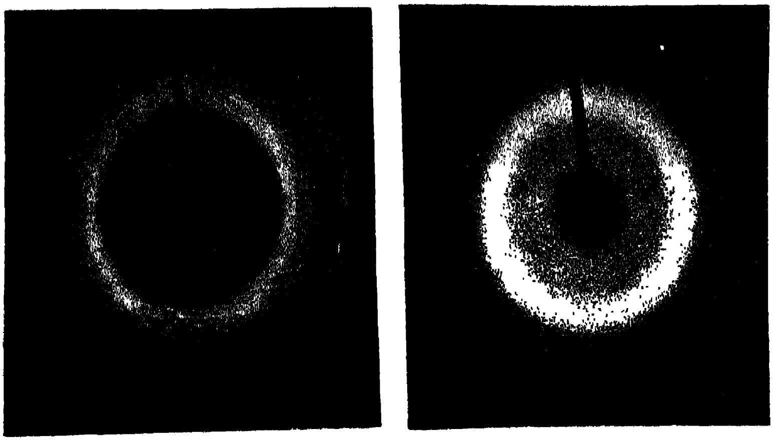


Fig. 3.

Fig. 1 Acenaphthene Fig 2. Fluorene Fig. 3. Diphenyl.

X—Ray Diffraction by Aromatic Hydrocarbons.

The data for these three substances are given below:

Diphenyl.	Dibenzyl.	Stilbene.
Monoclinic Prismatic.	Monoclin. Prism.	Monoclin. Prism.
$a=8\cdot 22$A	$a=12\cdot 82$	$a=12\cdot 42$
$b=5\cdot 69$	$b=6\cdot 18$	$b=5\cdot 73$
$c=9\cdot 50$	$c=7\cdot 74$	$c=16\cdot 0$
$\beta=94^\circ 8'$	$\beta=116^\circ$	$\beta=114^\circ$
$Z=2\cdot$	$Z=2.$	$Z=4\cdot$

Table III gives the values for the prominent lines in the powder pattern as well as for the rings in the liquid patterns.

Table III.

Substance.	Powder.		Liquid.		Intensity.
	λ in A.	Intensity.	θ in degs.	λ in A.	
Diphenyl ...	9·64	Med. str.	18·8	4·70	Strong
	4·63	Strong			
	3·88	Med. str.			
	3·17	,,			
Dibenzyl ...	4·78	Med, str.	17·9	4·95	Strong
	4·28	,,			
	3·78	Weak			
	3·24	,,			
Stilbene ...	4·62	Strong	9·9	8·96	Weak
	3·88	,,	17·9	4·95	Strong
	3·17	Med. str.	...	(3·8)	Limit of scattering

Diphenyl.—The crystal structure of diphenyl is very similar to those of fluorene and phenanthrene. The length of the molecule lies along the c—axis, and the plane of the molecule, if similar to that of naphthalene, should be nearer the bc plane. Here also the thickness of the molecule will be $\frac{a \sin \beta}{2} = 4{\cdot}10$ A approximately. The length of the molecule is 8·2A.

The liquid pattern consisted of a single fairly sharp ring almost in the same position as that of benzene (4·7A). There was general scattering extending to some distance outside the ring as for benzene. Since the length of the molecule lies along the c—axis, and since the molecule possesses a centre of symmetry between the two rings, the 002 reflection (4·73A) is very strong in the crystal. This corresponds very closely with the liquid spacing. Further, since the length of the molecule is 9·5A. the area of cross-section will be nearly

$$\frac{218\text{A}^3}{9{\cdot}5} = 23.0$$

so that the average dimension in the plane and perpendicular to it will be $\sqrt{23}$ or 4·8A, which equally well agrees with the liquid spacing.

It should be noted here that dibenzyl could be considered only as a singly substituted benzene derivative, and the absence of two rings is not surprising. The liquid pattern differs widely from those of fluorene and phenanthrene which show two rings in a dense background, though crystal structure data showed great similarity between the three molecules.

Dibenzyl.—Crystal structure data show this molecule to lie in the cell with its length along the a—axis. In other respects it is quite similar to diphenyl. Its length is about 12·8A so that the area of cross-section of the molecule will be :

$$\frac{182 \times 1{\cdot}66}{1{\cdot}105} \times \frac{1}{12{\cdot}8} = 21{\cdot}4 \text{ A}^2$$

and the average value for each dimension will be $\sqrt{21{\cdot}4} = 4{\cdot}6$A. Since the value for the length is not quite certain and since the density diminishes on melting, the value ought to be higher in the liquid.

The liquid pattern is very similar to that of diphenyl, but the ring is a little smaller, but not in proportion to the increase in length of the molecule. This reminds one of the case of longchain aliphatic hydrocarbons. The value of the spacing 5A is very near the value obtained for benzene or for diphenyl.

Stilbene.—The shape of the molecule is similar to that of dibenzyl. But there are four molecules per unit cell, and two molecules act together as one unit. The length of the molecule which lies along the *a*—axis is 12·4A, a little smaller than that of dibenzyl. The area of cross-section is very nearly the same as in the latter.

The liquid pattern shows a great resemblance to that of dibenzyl, and the ring is in practically the same position. In addition, an inner faint ring (about 9A) could also be observed. This is to be expected since stilbene differs from dibenzyl in possessing a double bond, and hence the distribution of the molecules will be influenced thereby, leading to the formation of the inner ring, as we see in associated liquids like acetic acid, ethyl alcohol or phenol.[23]

It is certainly noteworthy that none of the substances, dibenzyl or stilbene show the outer ring at about 3-4 A found in the other derivatives. This is because the former are not di or tri-substituted and hence the distribution of molecules follows quite a different line.

It will thus be evident from a consideration of these related hydrocarbons in the liquid state that the shape of the molecule and its anisotropy which influences the distribution of the neighbouring molecules are the main factors influencing the X-ray diffraction patterns. Conversely, the latter method is useful in deciding the shape, size and orientation of the molecules in the liquid state.

6. *Summary.*

(1) A comparison of the powder and liquid X-ray patterns has been carried out in the case of seven representative aromatic hydrocarbons whose crystal structure has been partially or fully analysed, *viz.*, naphthalene, acenaphthene, fluorene, phenanthrene, diphenyl, dibenzyl and stilbene in addition to hexamethyl benzene previously studied by the author.

(2) Acenaphthene, naphthalene, fluorene and phenanthrene show two rings in the liquid state as against diphenyl, dibenzyl and stilbene which show only one. This is accounted for by the difference in arrangement of neighbouring molecules or impedence to free rotation or vibration introduced by *o* and *m* substitution in the aromatic nucleus. Stilbene shows also a faint inner ring probably due to association.

(3) The origin of the liquid diffraction patterns is discussed in relation to the dimensions of the molecules as derived from crystal structure data.

In conclusion, the author desires to thank Sir C. V. Raman, F.R.S., for his keen interest in this work, and helpful criticism.

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Bibliography.

(1) Debye and Scherrer, Gott. Nachr, 1916, 22. Interference of X-rays employing amorphous substances.

(2) Huckel, Phys. Zeit., **22**, 561 (1921). Scattering of X-rays by anisotropic liquids.

(3) Keesom and Smedt, Proc. Roy. Soc., Amster., **25**, 118 (1922); and **26**, 112 (1923). Diffraction of X-rays in liquids.

(4) Hewlett, Phys. Rev., **20**, 688 (1922). X-ray scattering by carbon, lithium, liquid benzene, mesitylene and octane.

(5) Raman and Ramanathan, Proc. Ind. Assn. Cult. Sci., **8**, 127 (1923). The theory of diffraction of X-rays by liquids, solutions and amorphous solids.

(6) De Smedt, Bull. Acad. Belg., **10**, 366 (1924). Diffraction of X-rays in liquids.

(7) Eastman, J. Amer. Chem. Soc., **46**, 917 (1924). X-ray diffraction patterns form crystalline and liquid benzene.

(8) Prins, Physica, **6**, 315 (1926). Diffraction of X-rays by mercury.

(9) Zernike and Prins, Z. f. Phys., **41**, 184 (1927). Bending of X-rays in liquids as an effect of molecular arrangement.

(10) Raman and Sogani, Nature, **120**, 514 (1927). X-ray diffraction in liquids.

(11) Sogani, Ind. J. Phys., **1**, 357 (1927). X-ray diffraction in liquids.

(12) Sogani, Ind. J. Phys., **2**, 97 (1927). Further studies on X-ray liquid diffraction.

(13) Stewart and Morrow, Phys. Rev., **30**, 232 (1927). X-ray diffraction in primary normal alcohols.

(14) Katz, Z. f. Phys., **45**, 97 (1927). Influence of form and polarity of the molecule on the X-ray spectra of liquids.

(15) Herzog and Jancke, Z. f. Phys., **45**, 194 (1927). Comparison of X-ray patterns of organic substances in the solid and liquid state.

(16) Stewart and Skinner, Phys. Rev., **31**, 1 (1928). X-ray diffraction in primary normal alcohols and their isomers.

(17) Morrow, Phys. Rev., **31**, 10 (1928). Diffraction of X-rays in liquid normal fatty acids.

(18) Carl Drucker, Phys. Zeit., **29**, 273 (1928). The diffraction of X-rays in liquids.

(19) Katz and Selman, Z. f. Phys., **46**, 392 (1928). Part II of paper (14).

(20) Krishnamurti, Ind. J. Phys., **2**, 355 (1928). The relation between chemical constitution and X-ray diffraction in liquids.

(21) Sogani, Ind. J. Phys., **2**, 377 (1928). X-ray diffraction by carbon tetrachloride (liquid).

(22) Stewart, Phys. Rev., **31**, 174 (1928). X-ray diffraction in liquid normal paraffins.

(23) Krishnamurti, Ind. J. Phys., **2**, 491 (1928). X-ray diffraction and molecular association in liquids.

(24) Stewart, Phys. Rev., **32**, 153 (1928). X-ray diffraction in liquids.

(25) Krishnamurti, Ind. J. Phys., **3**, 225 (1928). X-ray diffraction of crystal powders and liquids in relation to their constitution.

(26) Stewart, Phys. Rev., **32**, 558 (1928). Theory of X-ray diffraction in liquids.

(27) Prins, Nature, **123**, 909 (1929). X-ray evidence for intermolecular forces in liquids.

(28) Krishnamurti, Ind. J. Phys., **3**, 507 (1929). X-ray diffraction in liquids and solutions and the molecular structure factor.

(29) Prins, Z. f. Phys., **56**, 517 (1929). On the diffraction of X-rays in liquids and solutions.

(30) Mark, Z. f. Phys., **54**, 505 (1929). Theory of X-ray diffraction in liquids.

(31) Stewart, Phys. Rev., **33**, 889 (1929). Diffraction of X-rays in benzene, cyclohexane and certain of their derivatives.

(32) Krishnamurti, Ind. J. Phys., **4**, 449 (1930). X-ray diffraction in liquid hexamethyl benzene.

Anomalous Diamagnetism and Crystal Structure

By

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(Received for publication, 10th December, 1929.)

1. *Introduction.*

In two famous memoirs on "Thermomagnetische Eigenschaften der Elemente", Kotaro Honda and Owen[1] had observed the remarkable phenomenon that graphite shows a rapid diminution of susceptibility with temperature. Thus graphite with a value of about -4·9* sp. χ at atmospheric temperature falls down to about $-1{\cdot}2$ at 1000° C. Bismuth and antimony having an anomalous diamagnetism of about $-1{\cdot}3$ and $-0{\cdot}8$ at atmospheric temperatures, show a decrease on heating and a sudden diminution on melting.

Bismuth and antimony are also anomalous in that their diamagnetism in combined state is many times smaller than in the solid state. Graphite in particular and also the two other elements exhibit a high degree of anisotropy. It is also a curious fact that the other allotropic modifications of carbon have a very small susceptibility compared with that of graphite. Is anomalous diamagnetism then not an atomic property ?

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[1] Kotaro Honda and Owen, Ann. der. Phys. **32**, 1027, 1910 and **37**, 657, 1912.

* In the paper, the susceptibilities are throughout expressed in the unit of 10^{-6} and should be multiplied by the factor.

Closely connected with the diamagnetic property of graphite and amorphous carbon is the X-ray phenomenon observed by Debye and Scherrer, that whatever may be the form of amorphous carbon, the diffraction maxima occur at about the same angle as in the case of graphite but much more diffuse. We have also the experiments of Asahara[2] on graphite and colloidal graphite. He has observed that when graphite was colloidalized for a number of days and the fine particles were investigated, there was no powder pattern, but only a broad diffuse ring as liquids give near their critical temperature. If anomalous diamagnetism is due to crystal structure, then a decrease should be observed on colloidalization according to X-ray evidence.

We have already the hypothesis of Ehrenfest[3] that the high diamagnetism of bismuth is due to the large electron orbits in the crystal lattice and that of Raman,[4] that the same hypothesis might explain the diamagnetism of graphite.

It was thus thought important to examine the diamagnetism of the colloids of anomalous diamagnetics. There is no literature on the subject, but there is a single observation of Honda and Owen in the memoir referred to, where the diamagnetic susceptibility of "regulus" bismuth is given as 1·34 and that of colloidal bismuth 0·495. This curious fact has not been noted at all; probably the discrepancy was thought to be due to impurities as in many magnetic observations.

It is hoped that a thorough investigation of the diamagnetism of the colloids, the anisotropy, the electrical and the thermal conductivities in the different directions of the crystals may serve to elucidate the problem of anomalous diamagnetism completely. The present paper only deals with the first property of the three anomalous diamagnetics: graphite, bismuth, and antimony.

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[2] Asahara, Sc. Papers of the Institute of Physics and Chemistry Research, Tokyo. 1, 23, 1922-23.

[3] Ehrenfest, Physica 6, 388, 1925.

[4] Raman, Nature, 123, 945, 1929.

2. *Experimental.*

The magnetic balance was of the Curie type, the torsion in a quartz fiber produced by the diamagnetic force being read by the deflection of the mirror as in the ordinary lamp and scale method. The deflections were kept small and in most cases the weight of water or standard substances was so adjusted, that the deflections were nearly equal and the retorsion method was not employed.

A large electro-magnet with inclined pole pieces gave the field. Precautions were taken to keep the current constant and obtain accurate values, the arrangements being similar to that the author employed during the investigation of vapours.[5]

When the diamagnetic property of highly anisotropic substances is determined, it is necessary to avoid the collision of the capsule with the walls of the balance chamber, as otherwise it leads to serious errors due to orientation of the crystals.

Special precautions were taken to avoid convection current and to secure accuracy. The susceptibilities are those obtained at atmospheric temperature, nearly 30° C.

(*a*) *Investigations on Single Crystals of Graphite.*

Crystal 1, weight 0·075 gram.

Crystal direction.	Deflection.	Sp. χ
C ⊥ F and horizontal	18	2·86 High field
C ⊥ F and vertical	17·5	2·78
C ∥ F	92·5	14·9

Magnetic anisotropy 5·27, mean sp. χ $\frac{a+b+c}{3}$; 6·85

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[5] Vaidyanathan, Ind. Jour. Phys., 2, 135, 1927.

Crystal 2, weight 0·16 gram.

Crystal direction.	Deflection.	Sp. χ.
C ⊥ F	7·3	2·7 Low field.
C ‖ F	49	18·09

Magnetic anisotropy =6·7, mean sp. χ=7·83.

Crystal 3, weight 0·0501 gram.

Crystal Direction.	Sp. χ.	
C ⊥ F	3·11	Low field,
C ‖ F	17·0	

Magnetic anisotropy=5·5 mean sp. χ=7·94.

(*b*) *Determination of the Absolute Value of Graphite Powder (purified).**

Weight.	Deflection.	Sp. χ.
·04 (graphite)	25 divisions.	
·083 (graphite)	47·5 ,,	
·310 (water)	23·5 ,,	
Empty capsule	2·5 ,,	
·550 (water)	46 ,,	6·12

Ceylon graphite was well powdered and purified in hydrochloric acid to remove iron. The purification was carried out a number of times until the filtrate gave no test with potassium thiocyanate. The graphite after purification was dried thoroughly and used in subsequent investigations. The absolute value of pure graphite was determined in comparison with that of water.

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* Due to the fact that the author was appointed as reader in the Annamalai University, though the work was started at Calcutta, it was carried out in the University Laboratories. The electric source in the latter being only a battery of 110 Volt, the observations on different days were not constant due to the fluctuations of the battery charge. It therefore became necessary to repeat the standard substance, the 'regulus' and the colloid at every observation to avoid uncertainties. This has been done using a sensitive ammeter.

With a view to thoroughly examine the various effects on graphite, the following investigations were made.

(c) *Influence of mechanical disturbances.*

The capsule was so arranged that it was not free to orient about its own axis.

1.	On pressing, the specific susceptibility was	3·9
2.	On tapping in a magnetic field of about 20,000 gauss ...	2·12
3.	When the capsule was turned at right angles to that in position 2 ...	7·0
4.	After disturbance ...	4·3

(d) *Influence of colloidalization.*

The purified sample of graphite was then mechanically colloidalized. The powder was treated with a one per cent. solution of tannic acid and finely powdered in an agate mortar for a number of days. This was then stirred continuously for about a fortnight with a mechanical glass stirrer fitted with paddles. These were then allowed to settle for about a week. The different layers were taken off and centrifuged or sometimes allowed to sediment for weeks. The weights obtained were generally small being about 0·01 to 0·02 gram and the susceptibility of these different specimens was determined.

Weight.	Deflection.	Sp. χ.
0·025	20·5	4·98 powder.
0·029	16·5	3·2 0·8μ
0·013	4·7	2·2 very violent motion in the high power microscope.
0·021 ?	2·5?	2 > 1 One month sedimentation.
[6] 0·013	+1	? Spongy mass decanted and evaporated.

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[6] In this case it may be that the apparent paramagnetism is due to the absorbed oxygen from the atmosphere, since the small weights are obtained by slow long and cumulative processes. Similar observations have repeated during 2 or 3 independent colloidalizations.

To determine the source of error due to tannic acid, its susceptibility was determined.

0·05 3·75 0·75

Since only a one % solution was employed the susceptibility due to the whole weight of the tannic acid was 0·075 and hence too small to affect the value of graphite to any appreciable extent.

(*c*) *Cane sugar charcoal, purified (amorphous).*

Weight.	Deflection.	Sp. χ.
0·15	11·3	0·60
0·209	14·9	0·57
		mean 0·585

In order to test the ash content of sugar carbon 0·3 gram of the substance was heated and gave 0·0005 gram of ash. This is 0·12% ash content and gave no test for iron.

(*f*) Another important point that suggested itself was that if the microcrystals orientated in the field, the decrease of susceptibility might be apparent and purely a directional effect. In order to test this point a small lump of graphite was mixed with canada balsam, and the susceptibilities of the mixture and constituents were measured separately. The canada balsam holds together the small particles and does not allow any orientation. The following results were obtained.

Weight.	Deflection.	
0·063	64	graphite.
0·107	70	mixture with canada balsam.
0·340	49·5	canada balsam.
0·500	73	canada balsam.

In the mixture, 0·044 gram of canada balsam causes a deflection of 7 mm. as in the pure substance and hence the effect is purely additive and there is no orientative effect of the micro-crystals.

(*g*) *Effect of heat.*

In order to examine qualitatively, the effect of heat on pure powdered graphite, the specimen was heated up to about 400°C the susceptibility showing a decrease. This was in conformity with the observations of Honda and Owen.[7] The object in repeating the same was only to examine if the decrease they observed was due to impurity, since I took special precautions to purify the substance.

(*h*) *Experiments on antimony and its colloids.*[8]

Weight.	Deflection.	Susceptibility.	Physical state.
0·38	46	0·72	Water.
0·19	25	0·779	' Regulus ' Kahlbaum
0·24	29	0·707	6μ Antimony.
0·32	28·5	0·535	150μμ } Compared
0·297	34·5	0·72	Water } immediately.
0·0225	0		Ultra-microscopic. ,,
0·023 (regulus)	4·2	0·779	

(*i*) *Experiments on antimony compounds.*[9]

Compound.	Mol. sus.	Ionic. sus.
$SbFe_3$	45·5	Sb^{iii}26·3
$(C_6H_5)_3Sb$	182·2	Sb^{iii}25·9
$(C_6H_5)_3Sb(OH)_2$	238·3	Sb^{v} 66·9

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[7] *Loc. cit.*

[8] Antimony and bismuth were colloidalized as graphite, but the process was continued much longer.

[9] Tables Annales, Internationale de constantes, Vol. V, Part I, 797, 1925.

(*j*) *Experiments on bismuth and its colloids.*

Weight.		Deflection.	Susceptibility.	
0·179	Bismuth "regulus"	8·5 low field	1·17 (mean)	Compared immediately.
0·342	Water	11 " "		
0·179	Bismuth "regulus"	41 high field		
0·342	Water	51 " "		
0·081	(·5μ) bismuth	10·5	0·598	"
0·081	"Regulus" bismuth	20·5	1·17	
0·120	Arced in distilled water [10]	7·5	0·286	"
0·120	"Regulus" bismuth	30	1·17	

(*k*) *Experiments on bismuth compounds.*

Substance.	Sp. χ.	Molecular χ.	Ionic sus.
Bismuth nitrate, $5H_2O$	0·329	159·2	13·1 Bi^{iii}
Bismuth trisulphide	0·284	144·3	45 "
Bismuth selenide	0·284	184·9	54 "
[11] $Bi(C_6H_5)_3$		106·9	40·6 "
[11] $(C_6H_5)_3Bi(NO_3)_2$		254·5	69·8 Bi^{v}

3. *Discussion of Results.*

The two theories, one that of Schrodinger and the other of Langevin, do not explain the anomalous diamagnetism. According to the former theory, the electrons are considered as free as the molecules of a gas and the expression for the volume susceptibility is $\chi = \frac{1}{3}\frac{ne^2\lambda^2}{m}$ Simple calculation shows that this is far too small for elements having small conductivities. Only in elements having a very high conductivity does the contribution come to nearly of the same order as that due to Langevin theory. Of all the metals it is curious that antimony and bismuth have the smallest conductivity and graphite has a conductivity of the same order as bismuth. The following are the conductivity values at atmospheric temperatures:

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[10] In the case of arced bismuth it is possible that such a low value might be due to the formation of the oxide and the fine powder consisting of the mixture.

[11] Tullio Gnessato et Maria Binghinotto, Atti. R. Inst. Veneto, 72, 1515, 1914, and Tables Internationale de Constants, Vol. IV, part 2, 667, 1922.

Graphite[12]	$0{\cdot}002 \times 10^6$	Best specimen. Values vary.
Bismuth	$0{\cdot}0084 \times 10^6$	
Antimony	$0{\cdot}025 \times 10^6$	
Copper[13]	2×10^6	

The theory of free conducting electrons, so successful in explaining conductivity, does not then seem to be applicable in this case. In the case of graphite, Koenigsberger [14] has measured the thermal conductivity also, obtaining a value of 0·85 (Cal/Cm. sec. °C.) which is nearly equal to that of copper and the substance therefore does not obey the law of Wiedemann and Franz.

According to Langevin theory, the diamagnetism is atomic and hence cannot explain the thermal, colloidal and chemical changes of diamagnetism.

But as suggested by Ehrenfest [15] and Raman [16] if we attribute the high diamagnetism to the lattice electron orbits, we may understand these phenomena more clearly.

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[12] Roberts, Phil. Mag., 23, 158, 1913. The paper contains a beautiful account and summary of some of the properties of graphite.

[13] The value of copper is given only for comparison.

[14] Koenigsberger and Weiss, Ann. der. Phys. 38, 122, 1910.

[15] *Loc. cit.*

[16] *Loc. cit.*

(1). *The Different Valencies of Graphite and its X-ray Structure.*

The structure of graphite has been ascertained by X-ray analysis, (see Bragg, X-rays and Crystal Structure). The distance between the vertical layers (*i.e.* along the *c* axis, is 3·40A and between the carbon atoms in the horizontal layers is 1·5A. The basal planes or planes of cleavage are hexagons as in the case of the benzene ring and according to Bragg, there is a concrete existence for these rings in graphite. The crystal structure is rhombohedral. But here the four valencies of graphite unlike those of diamond are differentiated into a 3 + 1 valency. The single or the fourth valency is supposed to be directed upwards between the different layers and this is long and weak. The cleaving and lubricating tendencies of graphite are supposed to be due to this weak mobile bond. Thus a change in the shape of the atom is accompanied by the change in the crystalline form.

As mentioned in the introduction, the amorphous carbon derived from different sources showed itself to be microcrystalline graphite.[17] The larger diffuseness in the X-ray patterns of the amorphous variety as compared with that of graphite is explained by Debye and Scherrer as analogous to the case of a grating with a few lines in it, resulting in a smaller resolving power. But all forms of amorphous carbon have a susceptibility much smaller than that of graphite and so the susceptibility of graphite must depend also on the number of aggregate atoms in the microcrystal and this is what the present investigation on colloids indicates.

(2). *The 3 + 1 valency of graphite and its diamagnetism.*

According to the orbital theory of diamagnetism $\chi_A = -\frac{Nne^2}{6mc^2} r_1^{-}$, the letters having their usual significance.

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[17] Debye and Scherrer, *loc. cit.* (Bragg, X-rays and Crystal Structure).

If the fourth valency in graphite is directed between the different vertical layers, the diamagnetism in this direction (C⊥ F) must be the contribution from this orbit since the other 3 valencies are in the horizontal plane. The atomic susceptibility in this direction as determined by the average of the single crystal determinations is 35 and by simple calculation the radius comes out as 3·49A. Thus the magnetism-diameter 6·98A is twice the distance between the layers (3·40A) given by X-rays.

These facts can only be reconciled if this mobile bond goes to the alternate layer in its orbital circuit in the crystal. It is natural to suppose that this circuit is even longer, for we get the radius of the orbit from the assumption that it is circular according to the theory. If it is elliptic with the major axis || the *c* axis, it may comprise the atoms in 4 or 5 vertical layers, but it cannot be uniquely determined from magnetism. These single valencies must also be paired with those of atoms in the different layers, as otherwise a single valency orbit ought to exhibit paramagnetism in this direction, the diamagnetic contribution of the K shell being very negligible.

In the *ab* plane, the atomic diamagnetism reaches a very high value being 210 per gram atom. According to the orbital theory of diamagnetism, the contribution here is due to the three-valency electrons in this plane. Applying the orbital theory, the radius of the orbit comes out as 4·8A. The X-ray radius of each atom in this plane is 0·75A and therefore the total number of atoms enclosed by the orbit in the hexagonal plane is $\frac{4\cdot8^2}{0\cdot75^2}$ or 45 atoms. (The magnetic radius of atomic carbon in combination or from diamond is 0·59A). As graphite is typical of aromatics, such an orbit must comprise about 16 benzene rings. These orbits form a net-work of large equipotential surfaces in the crystal lattice in the plane of the hexagonal ring as truncated prisms. It is only necessary in this case to conceive of the valency electrons of the different atoms to touch each other and go round in unobstructed paths in the crystal lattice. These might also link the different molecular groups and thus form the conducting surfaces. Such a theory would indicate that in graphite when the macrocrystal groups are subdivided by heating[18] or colloidalization the diamagnetism would decrease. Also in the crystal, the resistance would increase considerably with temperature. The large increase of resistance has been observed by Roberts.[19] (Compare Robert's paper, page 174.)

(3). *The 2+3 Valencies of bismuth and antimony and their diamgnetism.*

In the case of bismuth and antimony, the contribution due to the core is larger than in carbon, due to the large number of electrons in the same, the atomic numbers being 51 and 83 for Sb and Bi respectively. The nearest rare gases with complete cores are Xe and Nt; but so far as I am aware, we have no experimental value for the diamagnetism of these gases. The core contribution may be obtained from the ionic values but these have also been found to vary and not sufficiently accurate for a quantitative basis.[20]

Regarding the two metals in the crystalline form, here also we have a case where in the crystal of the elements, there are two different groups of unequal valencies.[21] The existence of such unequal valency orbits would explain the high magnetic anisotropy and the anomalies in analogy with graphite. The crystal structures are also similar.

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[18] Honda, *loc. cit.*

[19] *loc. cit.*

[20] Further investigations are in progress for obtaining more reliable information.

[21] See also Bragg, X-rays and Crystal Structure, 5th edition, pp. 172, 189, 190.

Element.	*a*	a : c
Graphite (Rhombohedral trigonal.)	85° 6′	1 : 2·3
Bismuth ,, ,,	87° 34′	1 : 1·3
Antimony ,, ,,	86° 58′	1 : 1·32

It is also important to note that in graphite, bismuth and antimony crystals, even the coefficient of linear expansion is considerably large and this is strikingly in the *c* axis direction.[21]

The various effects observed in anomalous diamagnetics are thus in perfect agreement with their similarity in other properties.

4. *Summary and Conclusion.*

1. Colloids of graphite, bismuth and antimony have been magnetically investigated. These elements possessing respectively an anomalous diamagnetism of $61 \cdot 2 \times 10^{-6}$ (mean value of the purified graphite powder at atmospheric temperature) 250×10^{-6} and 93×10^{-6} for " regulus " at atmospheric temperature, showed a decrease of diamagnetism on colloidalization. This decrease was most striking in graphite and less in bismuth and antimony. In order to avoid chemical action these have been mechanically colloidalised and the centrifuged powder was dried and investigated.

2. The anisotropy of many single natural crystals of graphite was investigated. These varied slightly, but the best crystal gave an anisotropy of $1 : 6 \cdot 7$ when the *c* axis was $\perp$ and $\parallel$ to the field respectively.

3. In the compounds of bismuth and antimony, the ionic values are pointed out to be much smaller than in the crystal state—26×10^{-6} for Sb^{iii}; -66×10^{-6} for Sb^{v},

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[21] See also Bragg, X-rays and Crystal Structure, 5th edition, pp. 172, 189, 190.

-40×10^{-6} for Bi^{iii}, and -69×10^{-6} for Bi^{v} and -6×10^{-6} for carbon in compounds. The ionic values deduced from different compounds of bismuth and antimony were found to vary.

4. The decrease in colloidalization is interpreted as due to the existence of large electron orbits comprising groups of molecules in the macrocrystal, the valency electron circuits in these equipotential surfaces being also the conducting surfaces. Such a circuit in the crystal of graphite comprises a minimum of 19 benzene rings in the cleavage plane. From the magnetic standpoint, amorphous carbon may be considered as microcrystalline graphite and this is in conformity with the ideas of Debye and Scherrer, from their X-ray investigations of graphite and amorphous carbon.

5. The magnetic anisotropy of these elements is pointed out as due to the unequal valency groups (3+1) and (3+2) for graphite and for bismuth and antimony respectively. The anomalous diamagnetism of these elements is in perfect harmony with the similarity of crystal structure and other properties.

In conclusion, I have great pleasure in expressing my heartfelt thanks to Sir C. V. Raman for his keen interest in the problem and for providing the electro-magnet to carry on the investigations at the Annamalai University. I am no less indebted to the Vice-Chancellor, Mr. Ranganadhan for his kindness and encouragement.

Further Studies on the Raman Spectrum of Diamond.

BY

S. BHAGAVANTAM.

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ABSTRACT.

The Raman spectrum of an exceptionally clear and perfect diamond of 20 carats size is found to give a number of feebler lines of frequency shifts 1158, 1288, 1382, 1431, 1480 and 1585 on either side of the very intense principal line (1332) already reported. The one at 1158 is more prominent than others. There is a close correspondence between these values and some of the very weak infra-red absorption maxima of diamond given by Reinkober.

Various considerations indicate that the principal oscillation at 1332 and its components are optically inactive in ideal diamonds although in the more commonly occuring ones they may be rendered active by imperfections in crystal structure. The relatively strong absorption band at 1240 found by Robertson and Fox in some diamonds is explained on this basis. The complex band found by these authors as well as Reinkober in the region 2 to 6 μ may also be explained as due to the combinations of the principal frequency with its components and other weak active oscillations in the long-wave length region.

The results are discussed in relation to the data on specific heat of diamond. The existing theories of Debye and Born based on classical mechanics lead to results which do not agree well with the observed facts. Diamond is a homopolar crystal and a rigorous treatment based on the new mechanics appears necessary to explain the discrepancies.

The antistokes line corresponding to the principal Raman line of frequency shift 1332 has been observed and is found to be shifted from the exciting line by precisely the same amount.

The intensity of the principal Raman line is about 6 times as great as that of the 992 benzene line, an explanation for which is given from density considerations.

1. *Introduction.*

Of the various crystalline solids in which the Raman effect has been observed, diamond is probably the case of the greatest interest on account of the simplicity of its structure.[1] In a previous report[2] the author has recorded the results of the study of ten different samples of diamond. In all of them three distinct features were noticed; (1) Raman lines with frequency shift of 1332 wave numbers excited by each of the intense mercury lines, (2) a series of bands evidently in the nature of fluorescent radiation of which the most intense and best defined is at 4157 A.U., (3) a continuous spectrum extending from a fairly well defined limit at 4240 A.U. towards the red end of the spectrum. The intensity of all these features in the spectrum of diamond seemed to show remarkable variations from specimen to specimen, the Raman line being most intense and the fluorescent bands and continuous spectrum being weakest with clear white diamonds. In view of the fact that each of the carbon atoms in diamond is attached tetrahedrally to four others, it was thought that in addition to the Raman line with a frequency shift of 1332 wave-numbers there should be others which had been overlooked on account of their faintness, and a search for them was accordingly undertaken. Owing to the great kindness of the Maharajadhiraja of Darbhanga, the author had the opportunity of experimenting with two exceptionally fine diamonds, one perfectly flawless and of the purest white colour, about 20 carats size, and the other a clear but pale yellow diamond of extraordinary size (143 carats). A third smaller diamond belonging to Mr. N. C. Chunder previously used was also available for re-examination. The results described in this paper are based mainly on the spectrograms obtained with these diamonds. In all some 50 photographs, including those abtained in the earlier work, have been critically examined.

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[1] The earliest observations were by C. Ramaswamy, Nature, 125, 704 (1930); Ind. Jour. Phys., 5, 97 (1930).

[2] S. Bhagavantam, Ind. Jour. Phys., 5, 169 (1930). See also Robertson & Fox, Nature, 125, 704 (1930) and 126, 279 (1930).

2. *New Raman frequencies of diamond.*

There is no difficulty at all in photographing the 1332 principal Raman line, its intensity being so great that even with tiny diamonds an hour's exposure is usually enough. With diamonds of larger size such as those used in the present investigation, this line can be visually observed. The situation is quite different with regard to other fainter lines and experimentation is rendered difficult by several disturbing factors. Most of the diamonds examined have a pale yellow colour and the violet radiation of the mercury arc lamp is sensibly weakened in passing through them. Thus, except with unusually clear and colourless diamonds, the only mercury line which fully serves the purpose of exciting feeble lines is 4358 A.U. The cut of the diamond is such that all the facets send out the maximum of internally reflected light which carries with it a certain amount of continuous radiation of the mercury arc and presents an unfavourable background for the detection of feeble lines. In view of the long exposures involved and the extreme feebleness of the new lines, all attempts to use filters of various kinds in the path of the incident light proved unsuccessful. This difficulty is partly avoided by carefully adjusting the well focussed image of the diamond on the slit of the spectrograph in such a way that a minimum of the reflected light falls on it. A more serious difficulty is the presence of the continuous fluorescent radiation characteristic of the diamond which is superposed on the Raman lines. This feature cannot be got rid off as part of it is still excited by 4358 A.U. even after the elimination of 4046 A.U. In view of these difficulties it is found that an optimum exposure with the full mercury arc just enough to bring out the feeble lines on as light a background as possible is necessary to yield the best results.

On a spectrogram obtained after an exposure of about 6 hours with Mr. Chunder's diamond, a feeble line could be seen clearly at 4590·1 A.U., the intensity of which is only a few hundredths of that of the principal line. This is shifted by 1158 wave numbers from the 4358 mercury line. The corresponding line from 4046 falls at about 4245 A.U. which is in the region where the fluorescent continuous spectrum starts. Examination of the spectrograms obtained with this diamond indicated the existence of some feeble lines accompanying the principal line and rather close to it.* A well exposed spectrogram obtained with the white Darbhanga diamond showed these companion lines clearly. The exceptional clearness of this sample is a great advantage as it transmits the 4046 radiation quite freely. Besides the principal Raman line, a line corresponding to 1158 wave numbers excited by 4046 could be seen clearly on the plate. Various component lines accompanying the principal line, particularly on the long wave-length side have been observed. The frequency shifts of these lines are as follows : 1288, 1332 (principal line), 1382, 1431, 1480, 1585. The intensity of all the lines except 1332 is extremely low.

3. *Relation to Reinkober's absorption data.*

Reinkober [3] has investigated the infra-red reflection and absorption of diamond with notable results. His reflection measurements which were made with an exceptionally clear diamond showed that there was no detectable variation of the reflecting power throughout the infra-red region. Taking the observed refractive index of diamond for the red A 7600 line as 2·402 and extrapolating the values up to 20 μ on the basis of the usual dispersion formula involving a characteristic absorption in the ultra-violet at 1246 A.U., its reflecting power may be calculated from Fresnel's formula. The following Table shows the calculated values :

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* The author has recorded such a result in his previous paper with one of the diamonds. In subsequent investigations, these companion lines have appeared in almost every well exposed photograph.

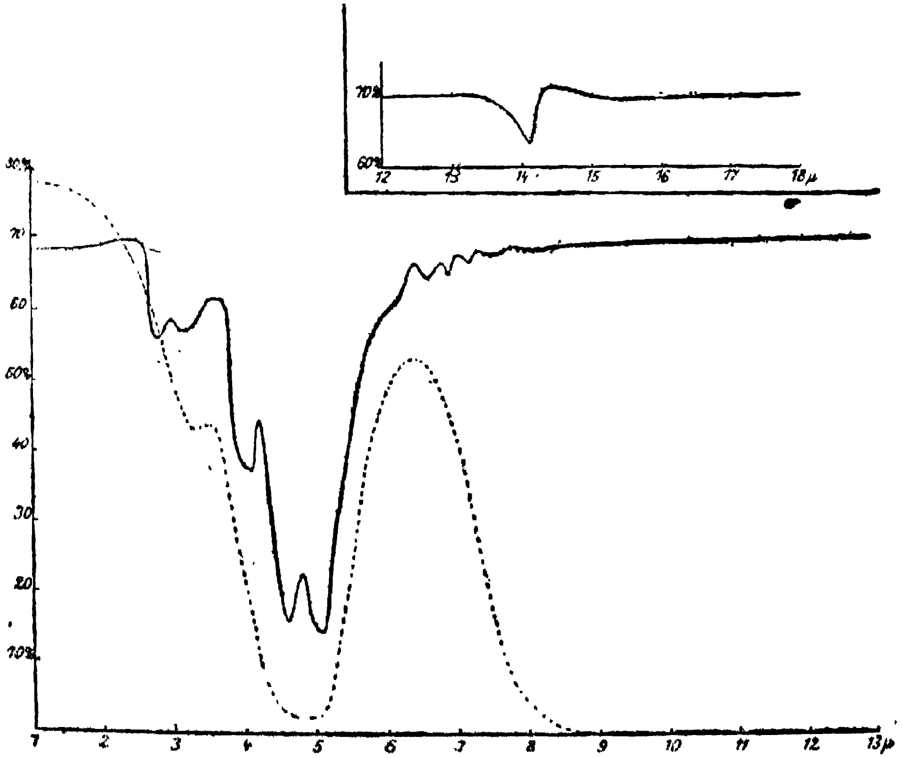
[3] Ann. d. Phys., 34, 343 (1911).

TABLE I

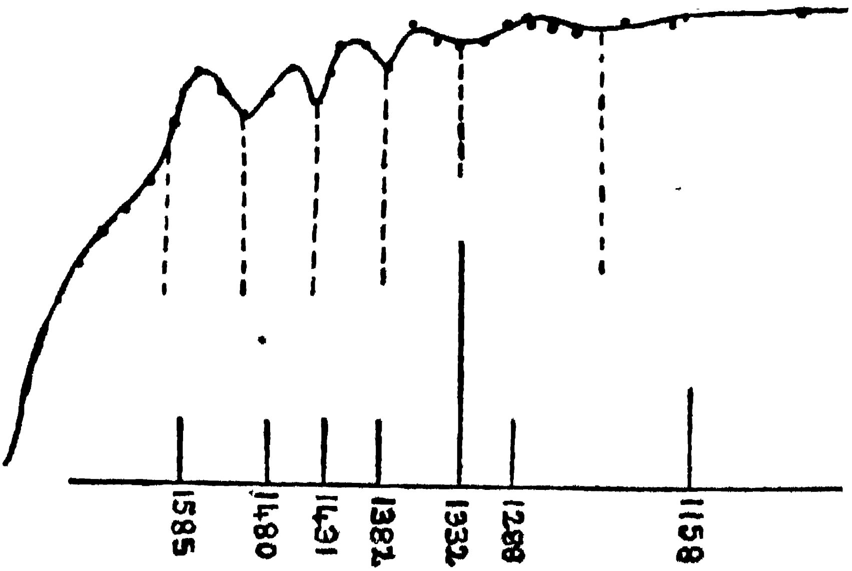
Reflecting power of diamond.

Wave-length in μ	·76	2	10	20
Refractive index	2·402	2·391	2·381	2·380
Reflecting power %	17·02	16·83	16·68	16·67

The values for the long wave-lengths are in close agreement with 16·5% as found by Reinkober throughout the region lying between 2 and 19μ. This suggests that there are no optically active frequencies in the infra-red region which could sensibly affect the refractivity of diamond. Such a view is in agreement with the fact that diamond is composed of neutral atoms linked by homopolar bonds in a crystal lattice possessing a high degree of symmetry.



The absorption measurements were made by Reinkober with another piece of diamond, 1·26 m.m. thick. His curve is reproduced above. He found a region of intense absorption showing pronounced maxima and minima between 3900 and about 1500 wave numbers, the prominent absorption maxima as read off from his curve corresponding to 3586, 3132, 2430, 2179 and 1962. At longer wave lengths, there is only a weak absorption ; but this fluctuates markedly, a series of maxima and minima being observed. Maxima of absorption are obtained at 1600, 1516, 1450, 1387, 1330 and 1235 wave numbers. Beyond this up to the remotest infra-red region investigated by him, he observed complete transparency except for a weak absorption at 710 wave numbers. It is very interesting that the principal Raman line at 1332 coincides very definitely with a point of maximum absorption in Reinkober's curves, and further, that the feeble companions to it observed in the spectrum of the white Darbhanga diamond are also represented in it. This is clear from Reinkober's curve enlarged and reproduced below. The dotted lines proceeding downwards indicate the absorption maxima, and their relation to the full lines representing the Raman spectrum on the same scale of frequencies is obvious from the figure.



We have now to consider the explanation of the fact that the Raman line 1332 which appears with great intensity in the scattered light with white diamonds is present only as an extremely feeble absorption in Reinkober's curve. There is no doubt that it corresponds to the principal mode of oscillation of the diamond lattice, for various properties such as its specific heat, thermal and elastic constants calculated theoretically assuming it to be the characteristic frequency agree reasonably with observation. The high intensity with which it appears in the spectrum of the scattered light with clear white diamonds, on the one hand, and the extreme feebleness with which it appears in the infra-red absorption on the other both suggest that it corresponds to an oscillation which is optically inactive, or at least would be inactive in an ideal diamond. Its feeble appearance in absorption would on this view be attributable to slight deviations of the crystal structure from complete perfection.

Reinkober's curve does not show any absorption corresponding to the Raman frequency of 1158 wave numbers. The reason for this is not clear. It is possibly also an inactive frequency but a more likely explanation is that it is a very weak and only feebly active frequency and as such is likely to have been missed in absorption. It is also to be noted that we do not find in the Raman spectrum, any line corresponding to the feeble absorption at 710 found by Reinkober. This does not however disprove its real existence as a feeble active oscillation frequency.

4. *Other infra-red absorption data.*

It is a very remarkable fact that the absorption of diamond seems to depend on the sample under examination. For instance the early observations of Julius indicated a strong absorption from about 3000 to 1500 wave numbers followed by a narrow region of transmission up to 1200. This result is similar to that obtained by Reinkober. On the other hand all wave-lengths beyond this region are found by Julius to be totally absorbed whereas Reinkober reports that they are very freely transmitted. More recent observations by Robertson and Fox indicate four absorption bands at 3353, 2438, 2086 and 1246 wave numbers. Although the three high frequency bands roughly agree with absorptions found by Reinkober, the absorption at 1246 is of a totally different character from the one found by him in this region. These authors find that such a result persists in seven different diamonds although they refer to one, which they call abnormal, showing absorption like that of Reinkober's diamond. Such remarkable variations are very significant and are perhaps closely connected with the already observed variations of the intensity of the principal Raman line in different specimens.

Some special characters of diamond which are of interest to us may now be mentioned. Different samples seem to show different values for their dielectric constants.[4] Pirani found in one case the very high value of 16·47, whereas other authors have reported values ranging from 5·5 to 8, while the value derived from the optical refractive index is 5·67. Under the action of light, diamonds become electrically conducting. This phenomenon is known as photoconductivity and was investigated by Gudden and Pohl.[5] According to Walter the absorption spectrum of diamond has bands at 4155A. U., the effect being marked in some crystals and feebler in others. The fluorescent band observed by the author at 4157 A.U. shows similar variations in that it is strong with blue diamonds but weak with colourless ones. All these facts suggest that under certain conditions the electrons of the diamond lattice pass into a mobile state and thus become active. The structural variations consequent on such a change will naturally result in the alteration of all or some physical properties of the substance; in particular those that have their origin in the optical electrons such as absorption, refractivity, conduction etc. It is reasonable to suppose that the infra-red oscillation corresponding to 1332 which is inactive under ideal conditions, ceases to be so in a great majority of the commonly occuring diamonds and begins to appear in absorption. The band observed by Robertson and Fox at 1246 is a broad one which covers within its' width, the observed Raman line at 1332 and its two companions on the long wave-length side at 1288 and 1158. The mean of the two latter frequencies is 1223, and can be reasonably identified with the absorption maximum observed by Robertson and Fox. It appears that the complex absorption observed by Reinkober as well as by Robertson and Fox in the region between 3500 and 1900 is the result of combinations between the various characteristic frequencies observed in the Raman spectrum and others in the long wave-length region beyond 1600. For example the three bands at 3353, 2438 and 2086 observed by the latter authors may be explained as 2 × 1332+710, 1332+1158, 1332+710. Better agreement can also be obtained by considering the other Raman frequencies lying in the neighbourhood of the principal line. That these combinational frequencies should give rise to the high intensities of absorption observed in this region is a difficulty which becomes less acute if we remember that the 1332 oscillation, although inactive, is intrinsically a very powerful one as a result of which it may give rise to prominent absorption when it combines with other weaker active frequencies. That the strong absorptions observed in diamond correspond to combinational frequencies rather than to fundamental vibrations of the lattice is seen to be a reasonable hypothesis when we recall Reinkober's observation that the reflecting power of diamond shows no increase whatsoever in the region of such strong absorption.

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[4] See Treatise on Inorganic Chemistry, J. W. Mellor, 5,781 (1924).

[5] Zeit. f. Phys., 17, 331 (1923).

It may also be noted here that Robertson and Fox report that they have not been able to locate the absorption at 710 observed by Reinkober.

5. *Specific heat of diamond.*

The case of diamond is of special interest as it is a classical example in which the heat content falls off very rapidly with decreasing temperature. From a very complete investigation of its specific heat at low temperatures Nernst[6] has shown that the value is not even a thousandth part of that predicted by Dulong and Petit's law. Many investigators have attempted to explain these remarkable variations on a theoretical basis. Einstein[7] was the first to formulate the quantum theory of specific heat on the assumption that the atoms are independent planck oscillators. He assumed that the important oscillation of the diamond lattice lies at about 900 wave numbers and successfully explained the observed phenomena at moderately high temperatures. The theory does not however account for the values at low temperatures. Subsequent attempts by Nernst and Lindemann[8], Simon[9], Schrödinger[10] and others are primarily based on the assumption of an empirical characteristic frequency of the lattice which yields the best agreement and have only met with partial success. The situation now is however slightly different as the Raman spectrum provides us with a precise knowledge of the fundamental frequency of oscillation viz., 1332. Taking this as the limiting frequency of the Debye spectrum, the specific heat may be calculated: values are compared with the observed data in Table II. The values of the Debye function are taken from his original paper.[11] For intermediate temperatures they are obtained by interpolation. Experimental values are taken from the work of Nernst, Lindemann and Weber.

TABLE II: Specific heat of diamond.

Temperature	48	86·5	92	205	209	220	283	306	331	358	413	479	879
C_v calculated	0·007	0·053	0·056	0·55	0·59	0·68	1·24	1·45	1·67	1·92	2·47	3·0	4·76
C_v observed	0·00	0·03	0·03	0·62	0·66	0·72	1·35	1·58	1·84	2·12	2·66	3·28	5·29

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[6] Ann. d. Phys., 36, 395 (1911)

[7] ,, , 22, 180 (1907)

[8] Zeit. f. Elektrochemie, 817 (1911)

[9] Sitz. der Preuss. Akad. Wiss., 33, 477 (1926)

[10] Handbuch der Phys., 10, 275 (1926)

[11] Ann. d. Phys., 39, 789 (1912)

[12] See M. Born, Dynamik der Kristall Gitter (1923)

It will be seen that the agreement is not quite satisfactory. In the low temperature region the observed specific heats are only about half the calculated values. It is interesting to note that the discrepancies are very systematic in that the observed specific heat is too low at low temperatures and too high at high temperatures and are therefore probably not due to experimental errors. The failure of the Debye theory noticed here is not surprising if we remember that the observed infra-red spectrum of diamond is not that presupposed by the theory. Whereas the Debye theory assumes a long and practically continuous series of oscillations ranging from zero to a limiting value where they all crowd up, the experimental results show that there are a certain number of discrete frequencies of which the one at 1332 is the most important but not the highest as the latter is also accompanied by weaker lines of still higher frequencies. Such remarkable phenomena which cannot satisfactorily be explained on the basis of the old quantum theory of specific heat show that we have in diamond a case where the classical mechanics completely breaks down.

6. *Interpretation of the new frequencies.*

A natural question that arises out of the foregoing considerations is regarding the origin of the new frequencies. The general theory of lattice oscillations developed by Born indicates 3N oscillations for a crystal containing N individual particles which divide up into 3S series. Three of these comprise the acoustic waves and are in the long wave-length region. Of the rest 3S—3 series which are known as the optical series, a certain number may fall in the ultra-violet and the rest in the infra-red region of the spectrum according as how many of the particles are electrons and how many are atoms. S is the number of particles in each basis group of the lattice. In crystals possessing elements of symmetry, some of the series may overlap, the actual number being reduced accordingly. The question now arises as to whether the observed Raman frequencies represent merely the heads of various different optical series or only the fine structure components of any one particular series. It seems difficult to accept either of these explanations as the number seems to be one too many in the former case whereas in the latter, although the more or less constant spacing of the various lines suggests such an explanation, they appear to be too far apart to constitute one series. On the whole it appears reasonable to suppose that the absorption extending from about 1100 to 1600 is in reality one fundamental oscillation and perhaps the only important and most powerful one associated with the diamond lattice. Its fine structure is due to some cause which is at present very obscure. It is however very significant that diamond is a homopolar crystal, and many of the curious phenomena observed above may receive an explanation based the modern theories of homopolar binding as developed by Heitler and London.

7. *Intensity, polarisation and other results.*

In the previous paper three components of the fluorescent band system were reported. In the present investigation, besides these which were found to occur in precisely the same positions, two others are observed making up five components in all. The wave-lengths of these bands are 4131, 4157, 4175, 4186 and 4196 A. U. The one at 4157 A. U. is the strongest and extends over 10 A. U. The fact that the fluorescent bands are observed in the clearest white diamond makes it clear that it does not arise from any extraneous impurities in the diamond.

The antistokes Raman line corresponding to the principal frequency has also been observed in two plates and is shifted by 1332 wave numbers from the exciting line, in absolute agreement with the shift of the stokes line. The intensity of the stokes line, on the basis of Boltzmann distribution law, should be 544 times that of the antistokes one at the room temperature ; the observed intensities are of the right order of magnitude.

The large Darbhanga diamond which was about 3 cms. in its linear dimensions afforded an opportunity of studying the absolute intensity and the state of polarisation of the principal Raman line. There is no doubt that the great intensity of this line is in part due to repeated internal reflections which enhance the total scattering of light within the diamond. To eliminate this source of error as far as possible, the diamond was immersed in distilled benzene contained in a cubical glass vessel. When this was done, it was noticed that the light yellow colour disappeared and the diamond seemed colourless, apparently as the result of the weakening of the internal reflections. The diamond fluoresced with a brilliant blue light when the image of the mercury arc was focussed on it by a glass condenser.

An aperture was placed in front of the diamond and the spectrum of the scattered light exposed for a known time. The diamond was removed and a series of graded exposures of the spectrum of the light scattered by benzene illuminated with the same aperture were given on the same plate. A visual comparison of the brightness of the lines on the plate showed that the diamond line is at least 6 times as strong as the principal 992 Raman line of benzene for equal exposures.

Such an extraordinary intensity of the principal diamond line is of interest, especially if we remember that the oscillations that are being compared have their origin in the forces that bind the carbon atoms in both cases. A simple explanation can however be given in terms of the densities of the scattering material. The density of diamond (3. 51) is much greater than that of benzene (0. 88) which means that the number of oscillators per unit volume is nearly four times larger in diamond than in benzene. Further in the spectrum of benzene, there are other lines besides the 992 which appear and need to be taken into account to consider the total energy of vibration of the carbon atoms. Taking these facts into consideration the intensity of the line obtained with diamond is not altogether surprising.

With a nicol interposed in the path of the scattered light, two photographs corresponding to the vertical and horizontal components are taken side by side on a plate with a view to estimate the state of polarisation of the line. * The results indicate that there is a considerable imperfection of polarisation, contrary to the observation of Ramaswamy who finds that the line is well polarised. It must be noted however that the work is rendered unreliable by the presence of internal reflections and repeated scattering, and more detailed investigations with diamonds of suitable shape are necessary to decide the state of polarisation with certainty and the variations it might show in different samples analogous to the variations in intensity.

In conclusion the author desires to express his best thanks to Prof. Sir C. V. Raman who kindly suggested the problem and gave many valuable suggestions and helpful criticism in the course of the work. Grateful acknowledgements are also due to His Highness the Maharajadhiraja Bahadur of Darbhanga whose kindness in loaning valuable diamonds made this research possible.

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* Correction due to the instrument is introduced in the times of exposures. See S. Bhagavantam, Ind. Jour. Phys., 5, 59 (1930)

38

Raman Effect with Cadmium Arc Excitation

BY

P. KRISHNAMURTI.

(Plate XXI)

(*Received for publication, 18th August, 1930.*)

ABSTRACT.

A cadmium arc with a 50% tin—cadmium alloy has been for the first time used for exciting Raman lines. The coloured substances, ferrous and nickel sulphates failed to show any line at about 10μ with any of the exciting lines, in conformity with previous results. In the case of sulphur crystals, with 5086 excitation all the frequencies previously reported were found. An additional very faint line ($\nu_G = 183$ cm^{-1}) was also found to to be present. The 4800 and 6439 radiations excited the three strongest sulphur frequencies with moderate intensity. The possibility of using the 6439 line for orange or red coloured substances is indicated.

In a previous communication,[1] the present author has noticed the absence of the inactive SO_4 frequency at about 10μ in the case of ferrous and nickel sulphate heptahydrates, using the crystal powder method and the 4358 mercury excitation. In order to exclude any possibility of the effect arising from absorption of the modified lines by the crystals, a source consisting of blue or blue-green radiations was found necessary. The cadmium arc hence proved very suitable since it gave two strong lines at about 4800 A and 5086 A as well as a very intense red line at 6439A.

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[1] Krishnamurti, Ind. J. Phys., *5*, 183 (1930)

The Cadmium Arc.

The primary difficulty in using this arc is the fact that molten cadmium wets glass or quartz, and when it cools is liable to burst the container. In order to obviate this difficulty, a 50% tin—cadmium alloy was used as recommended by Bates and Taylor.[2] An old quartz-mercury lamp of the Hewittic type was fused to a long quartz tube in the middle. This could easily be done in a carbon arc carrying a heavy current (about 20 amperes). The body and ends of the lamp were then wound with resistance wire, and a current of about one ampere was always sent through the resistance before and after the molten alloy of cadmium and tin in equal proportions by weight was poured in. The open end of the tube was then connected to a bottle of large capacity and then to a Cenco hyvac pump through a stop-cock. When fully exhausted the arc was struck after which the pump was stopped. The arc worked steadily afterwards with a current of about 6-7 amperes. A preliminary evacuation was necessary before the arc was started again after any long interval due to the presence of some minute leak in the system.

Since the arc was working at a high temperature, it was found necessary to cool the substance investigated in a current of running water. Otherwise, the arrangements were quite similar to those described previously for crystal powder work.[3] About 4 hours' exposure was usually sufficient using Ilford Panchromatic Soft Gradation plates, speed H and D 2000.

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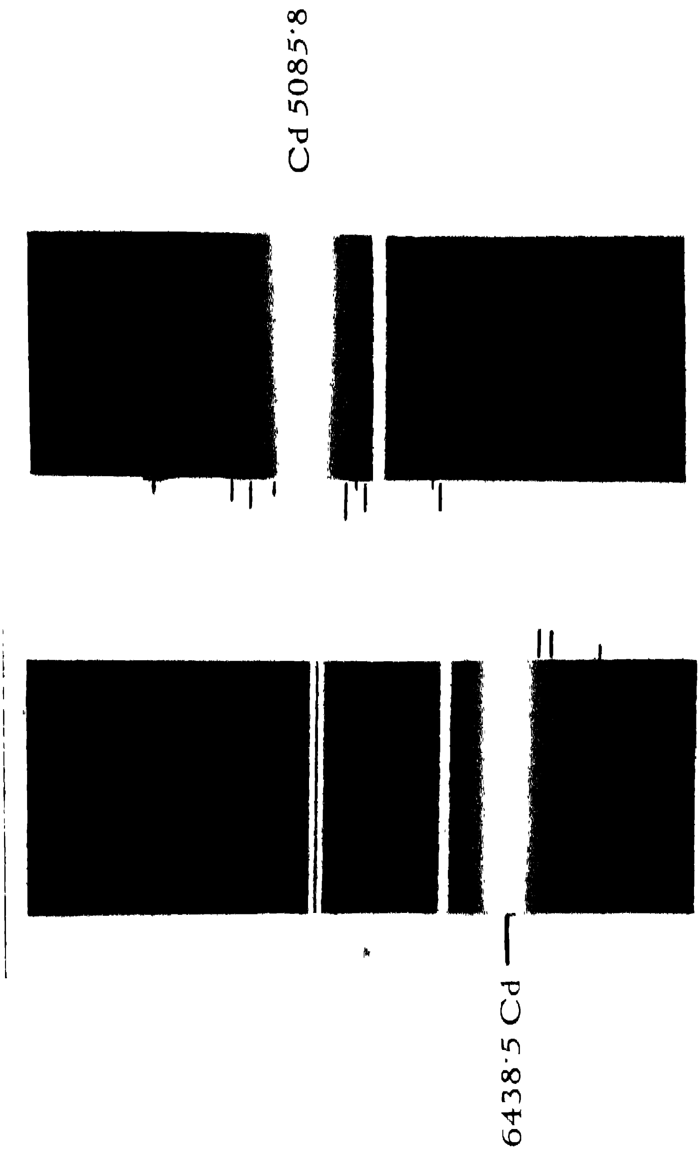
[2] Bates and Taylor, J. Amer. Chem. Soc., *50*, 771 (1928).

[3] Krishnamurti, Ind. J. Phys., *5*, 1 (1930).



Raman Spectra of Sulphur.

The maximum sensitiveness of the plates extends only up to 6600 A; hence, in special cases where the Raman lines occur at longer wavelengths, the plates should be specially sensitised. For this purpose Dicyanin A was found to be very suitable and Agfa Normal plates gave the best results. The solutions were prepared according to the well-known formulae.[4]

Results.

Ferrous sulphate crystals, $FeSO_4$, $7H_2O$, of Merck's reagent quality, consisted of fairly large transparent crystals, and so also were $NiSO_4$, $7H_2O$ crystals. Even though the incident lines were well-exposed, there was no evidence of any frequency at 10μ excited by any line. In the case of ferrous sulphate, a very faint broad line (corr. to 1018 cm^{-1}, excited by 4800 A) was of doubtful nature. The results obtained so far hence prove to be negative.

Sulphur crystals were also examined with some new results. The 4800 line was partially absorbed, but the green and red lines were completely transmitted by the substance. The Raman lines excited by 5086 A were fairly strong and those with the blue and red lines, of medium intensity. All the three strong Raman frequencies observed with the Hg green line[5] were present here also with all the different excitations. The following table gives the measurements for the observed lines.

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[4] Walter and Davis, Sci. Pap. Bur. Stand., *17*, 366 (1922).

[5] Krishnamurti, Ind. J. Phys., 5, 105 (1930).

TABLE I.

Exciting line λ in I.A.	Raman line λ in I.A.	Raman line ν in wave nos.	Δν	Intensity.	Assignment.
4799·91	4834·7	20678	150	Med. str.	ν_1
	4849·8	20614	214	,,	ν_2
	4910·0	20361	467	Weak.	ν_3
5085·83	4966	20131	474	V. weak.	$-\nu_3$
	5030	19875	218	Weak.	$-\nu_2$
	5047	19808	151	,,	$-\nu_1$
	5064	19742	85	V. weak.	$-\nu_0$
	5124·7	19508	149	V. Str.	ν_1
	5133·7	19474	183	V. weak.	ν_6
	5142·2	19441	216	Strong.	ν_2
	5198·7	19230	427	V. weak.	ν_5
	5209·6	19190	467	Strong.	ν_3
6438·47	6500	15380	147	Weak.	ν_1
	6527	15316	211	,,	ν_2
	6636	15065	462	V. weak.	ν_3

It will be seen that ν_0 has been obtained as before as the anti-Stokes component, the stokes line being hidden by the broadening of the incident line and diffraction effects due to over-exposure of the incident line. Another very faint line between ν_1 and ν_2 was found which was not reported previously (see ν_6 in Table I). Since ν_4 falls on an incident line it could not be observed.

Mercurous and mercuric chlorides previously examined with the Hg 4358 line[6] were also tried. They showed the strong line in both cases, excited by all the three cadmium lines. Longer exposures are however necessary to bring out all the fainter lines. It can be pointed out here that the cadmium arc is very suitable for studying intensity relationships between Raman lines with excitations ranging from 3000 A to 6500 A.

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[6] Krishnamurti, Ind. J. Phys., 5, 113 (1930).

Finally, the usefulness of the cadmium red line excitation could be considered here. This is visually the strongest line but photographically it is not very active. With dicyanin bathed plates it is possible to photograph the Raman spectra up to 8000 A which include lines of about 3μ. Another difficulty with this excitation is that according to the Rayleigh fourth power law, the red excitation should be very weak and further, the dispersion in those regions with glass spectrographs is very small. Nevertheless, when highly coloured substances have to be examined, *e.g.*, bromine, potassium dichromate or azobenzene, there is no alternative but to use such an excitation. It is possible that improved cadmium arcs with large illumination would shorten the otherwise long exposures necessary for these substances.

The author's thanks are due to Sir C. V. Raman, F.R.S., for his advice and interest in this work.

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Further Investigations on the Intensities of Lines in Raman Spectra

By

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(Received for publication, 21st August, 1930.)

Abstract.

The ratio of the absolute intensities of the displaced lines divided by that of the corresponding undisplaced lines has been determined in the case of Raman lines having shifts of 2853 and 800 wave numbers due to cyclohexane and those having shifts of 3080 and 990 wave numbers due to benzene. It has been found that the intensities of the Raman lines excited by ultra-violet lines are more than is indicated by the fourth power law relative to the visible lines, but Raman lines having greater shifts in frequency deviate more from the fourth power law than those having smaller shifts in frequency. For the 2853 line of cyclohexane, the deviation is 216% whereas for the 800 line the deviation is only 63%, the exciting lines being 4046 A and 3132 A. Similarly in the case of benzene, for the same two exciting lines, the Raman line having a shift of 3080 wave numbers shows a deviation of 267% whereas the 990 line shows a deviation of 51% only.

1. *Introduction.*

The results of measurement of intensities of Raman lines due to carbon tetrachloride have been reported recently[1] and it has been shown that the intensities of the Raman lines excited by the Hg line 3132 A. U. are greater than is indicated by the Rayleigh fourth power law relative to those excited by the line 4358 A. U. It could not, however, be said definitely whether intensities of the Raman lines of frequencies differing widely from each other obey the same law. Two more suitable liquids have therefore been investigated and the present paper gives an account of the measurement of relative intensities of Raman lines having large shifts from the incident lines.

2. *Determination of Photographic Sensitivity of the Plate for Different Wave lengths.*

The method developed by Merton and Nicholson[2] was employed in the present experiment also, to compare photographic intensities of different lines. As it cannot be assumed in the case of Raman lines with large shifts from the incident lines that the photographic sensitivity remains constant throughout the whole region between the exciting line and the Raman line, the photographic sensitivities of the plates used for photographing the Raman lines were first determined for different wave lengths. The old quartz wedge produced some disturbing interference bands whenever a continuous source of light was used. It was therefore necessary to keep a gap between the quartz plate on which the platinum was deposited and that used for protecting the film. Some other portion of the film was chosen as a wedge and it was again calibrated. This time, only two metal plates, one having an aperture about 1 cm. in radius and the other having about 48 holes drilled within the same area as that of the aperture, were used for calibration. The mercury line 4916 A. U. was used for determining the density per mm. of the wedge at different parts of its length. Two photographs on the same plate were taken with the aperture and the perforated metal plate placed successively in the path of the incident light. On the same plate four pairs of such photographs were taken, the time of exposure being different for different pairs so that the images due to the 4916 A. U. line were of various lengths, ranging from 1 mm. to 6·0 mm. Ilford Panchromatic Rapid Process plates were used and a cutting solution of potassium ferricyanide was used for the above experiments as previously. The new quartz wedge was found to have more uniform gradient than the old one, the density increasing gradually towards the thick end. The total density of the new wedge was slightly greater than that of the old one. The densities of the wedge for different wave lengths in the visible and ultra-violet regions were next determined. The densities of a 7 mm. long Hilger neutral tint wedge were also determined for different wave lengths in the visible region. As this Hilger wedge was used for determining the photographic sensitivity in the visible region, the results of calibration of this wedge are given in Table I.

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[1] S. C. Sirkar, Ind. J. Phys. 5, 159, 1930.

[2] Merton and Nicholson, Phil. Trans. A. Vol. 217, 237, 1917.

TABLE I.

λ in A. U.	5769	5460	4916	4358	4046
Density per mm.	0·60	0·615	0·630	0·785	1·088

The photographic sensitivities of Ilford Panchromatic H & D 2000 backed plates were then determined for different wave lengths. The positive crater of a carbon arc was used as the standard source of light. The density of the quartz wedge was so small that even when the length of the image of the slit was much smaller than that of the slit itself for the Hg line 3132 A.U., it increased rapidly towards greater wave-length and became equal (when corrected for magnification produced by the spectrograph) to the length of the slit in the neighbourhood of 3650 A.U. line. Hence two plates taken from a new packet of the abovementioned plates were calibrated—one for the visible region with the help of the neutral tint wedge and the other in the ultra-violet region with the quartz wedge. Mercury lines were also photographed on the same plates as comparison spectrum. A cutting solution of potassium ferricyanide was used to remove chemical fog and the lengths of images were measured under a Hilger travelling microscope. The relative absolute intensities in the spectrum of this standard source were calculated from Wien's Law taking T to be equal to 3650°. These values were corrected for dispersion of the spectrograph in the method given by Merton and Nicholson.[1] The relative ratios of I_p to I_λ where I_p is the photographic intensity and I_λ the corresponding absolute intensity for any wave length, were then found out for different wave lengths. The results are given in Table II.

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[1] Merton & Nicholson, *loc. cit.*

TABLE II.

λ in A. U.	I_p in arbitrary unit.	I_λ in arbitrary unit.	$\frac{I_p}{I_\lambda}$
5769	1148	353·5	3·22
5460	776	280·0	2·77
5030	669	176·0	3·80
4916	871	149·0	5·80
4619	1281	112·0	11·44
4557	816	106·0	7·70
4358	297	77·4	3·84
4217	225	60·0	3·75
4046	95	45·6	2·08
3437	60·0*	11·54	5·20
3212	13·0	5·89	2·21
3132	8·7	4·51	1·93

* From here the values for ultra-violet lines are given in another unit different from that for the visible region.

3. *Comparison of Intensities of Raman Lines.*

Raman spectra due to cyclohexane and benzene were next photographed on plates taken from the calibrated packet. The experimental arrangements were similar to those mentioned in the previous paper.[1] Just as in the case of CCl_4, it was found possible to avoid stray diffused light in the case of cyclohexane by focussing an image of the flat end of the quartz tube on the slit of the spectrograph, but in the case of benzene it was found impossible to avoid stray light with the same arrangements. This was probably because the refractive indices of carbon tetrachloride and cyclohexane are very nearly equal to that of fused quartz, whereas that of benzene is a little greater. The ratios of the undisplaced scattered lines for both the liquids were therefore determined from those of the incident lines, assuming the Rayleigh fourth power law to be obeyed. As a clean sheet of mica was used as filter between the lamp and the quartz tube, it was also used as a filter when ratios of incident lines were determined. In the case of cyclohexane, the undisplaced lines were also photographed on the same plate on which Raman lines were obtained and it was found that the intensity of the 3132 A.U. line was a little smaller than what would have been obtained from the Rayleigh fourth power law relative to the 4046 A.U. line. This discrepancy was so small that it could not be ascertained whether there was actual absorption in this ultra-violet region or some faint stray light superposed on the scattered light was responsible for the discrepancy. As two different wedges were used for determining photographic sensitivities in the visible and ultra-violet regions, the values of $\frac{I_p}{I_\lambda}$ for two wave lengths in these two regions were not directly comparable. It was however possible to compare the ratios of the absolute intensities of the displaced lines with those of the undisplaced scattered lines in the following way. Let I and I′ be the relative photographic intensities of two undisplaced scattered lines and let I_R and I'_R be those of the corresponding displaced lines. Let S_1 and S_2 be the ratios of photographic sensitivities at the undisplaced line to that at the displaced line in the case of the two wavelengths respectively.

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[1] S. C. Sirkar, *loc. cit.*

Then

$$\frac{I_R \times S_1}{I'_R \times S_2} \div \frac{I}{I'}$$

$$= \frac{\text{ratio of aboslute intensities of displaced lines}}{\text{ratio of absolute intensities of undisplaced lines.}}$$

Tables III and IV show the results obtained. In the second column of each of the tables are given the photographic intensities of the undisplaced lines calculated from those of the incident lines according to the 4th power law with respect to the longest exciting wave length in that table.

TABLE III.

Benzene.

Exciting line in A.U.	I for undisplaced line in arbitrary unit.	Wave-number shifts for Raman lines.	I_R for Raman lines in arbitrary unit.	S.
4358	1·0	990	38·4	0·50
		3060	4·06	1·00
4046	1·15	990	46·0	0·556
		3060	32·9	0·182
3132	0·494	990	19·0	0·875
		3060	25·5	0·37

TABLE IV.

Cyclohexane.

Exciting line in A. U.	I for undisplaced line in arbitrary unit.	Wave-number shifts for Raman lines,	I_R for Raman lines in arbitrary unit.	S.
4046	1·0	800	19·0	0·59
		2853	28·9	0·27
3132	0·427	800	8·90	0·88
		2853	25·0	0·43

The values of $\frac{I_R \times S_1}{I'_R \times S_2} \div \frac{I}{I'}$ can now be easily calculated for different Raman lines in the case of the two substances from the above tables. Calculated values are given in Table V, these quantities being given in the column β.

TABLE V.

Substance.	Exciting lines in A. U.		Wave-number shifts for Raman lines.	β
	λ_1	λ_2		
Benzene	4358	4046	990	1·15
			3060	1·29
	4046	3132	990	1·51
			3060	3·67
Cyclohexane	4046	3132	800	1·63
			2853	3·16

4. *Discussion.*

It is quite evident from the results given in Table V that the Raman lines of larger frequency shifts deviate more from the fourth power law than those of smaller shifts. Had the Raman lines due to λ_2 obeyed the inverse fourth power law with respect to those due to λ_1, we would get for the value of β, only 1·0. If frequencies of Raman lines were considered instead of those of exciting lines, β would be very slightly differet from 1·0. The deviation from the fourth power law is as great as 267% in the case of one of the Raman lines. Recently Manneback [1] has put forward a theory of the inten-

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C. Manneback, Zeit. f. Phys., 62, 224, 1930.

sity and polarisation of light scattered by diatomic molecules. According to him the intensities of Raman lines depend on the change in the mean anisotropy and optical polarisability with that in the distance between the nuclei, whereas those of undisplaced lines depend on the total anisotropy and optical polarisability of the molecules. The large deviation from the fourth power law may be due to these changes in optical polarisability and anisotropy being quite different for different exciting lines and also for different modes of vibration, and different Raman lines therefore may obey different laws.

The author's heartfelt thanks are due to Prof. Sir C. V. Raman, F.R.S. for his kind suggestion and guidance.

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40

The Polarisation of Raman Lines: Some Hydrocarbons.

By

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(*Received for publication, 16th September, 1930.*)

ABSTRACT.

The results of a study of the polarisation characters of the Raman lines in benzene, cyclohexane and pentane are described. The lines with a frequency shift of 992 in benzene and 800 and 992 in cyclohexane are distinguished for their almost perfect polarisation. It is suggested that these represent inactive oscillations which is supported by the fact that the 992 of benzene appears only weakly and the 800 and 992 of cyclohexane not at all in the respective infra-red absorption curves. In all the three compounds, the different components of the characteristic hydrogen frequency appear with very different degrees of polarisation, the more intense components being usually the better polarised. Benzene is distinguished from the two other compounds by exhibiting several lines which show no detectable polarisation.

1. *Introduction.*

In an earlier paper [1] the author has described the results of a systematic investigation of the polarisation of lines in the Raman spectra of some simple compounds. The study at the time was however confined to such compounds as are marked by their simplicity of structure and certain striking similarities are shown to exist between the Raman lines arising from molecules having analogous structures. It is thought desirable to extend the investigations to at least some typical compounds chosen from the very vast field of organic chemistry and particularly to those Raman lines which have been given a definite origin. It is well known that these compounds give very complicated Raman spectra the interpretation of which is still very obscure even in relatively simple cases like benzene. Extensive investigations by Venkateswaran, Dadieu and Kohlrausch and others have shown that a study of the Raman spectra affords a powerful means of elucidating various points which are of interest to the structural chemist. One of the most fascinating phenomena is that certain lines, while preserving their individuality, undergo remarkable variations of intensity and position as we pass from compound to compound in any particular group or from one well defined chemical group to another. There has been however very little work done so far from the view point of polarisation. In the present paper three typical liquids, *viz.*, benzene and pentane representing the aromatic and the aliphatic classes of compounds respectively and cyclohexane, a transition between them, have been chosen and an investigation made of the polarisation characters of their Raman spectra.

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[1] Ind. Jour. Phys., 5, 59 (1930).

2. *Experimental arrangements.*

All the three liquids were of Kahlbaum's make and have been repurified by slow distillation in vacuum. The liquids were contained in large double bulbs and illuminated by the light of a mercury arc lamp focussed on them by means of a powerful glass condenser. For liquids which are available in large quantities such an illumination affords an ideal arrangement in which the reflected light is almost completely eliminated. All the polarisation pictures were taken without the use of any lens in the path of the scattered light. A large two prism glass spectrograph supplied by Adam Hilger is made use of in the investigation. The details of the method and the corrections employed are the same as those described by the author in his earlier paper.

3. *Polarisation of the Raman lines.*

The results obtained with the three liquids are given in Table I. I represents the relative intensity of the line and ρ the depolarisation defined as the ratio of the weaker to the stronger component in the scattered light observed normal to the direction of the primary beam. The spectrograms are not very intense and show only the more prominent lines. With well polarised weaker lines and almost completely polarised strong lines the weak component is either seen very feebly or not at all in which case an upper limit for the depolarisation factor is given.

TABLE I.

Polarisation of Raman lines

Benzene	ν	607	852	992	1181	1597	3046	3060			
	I	8	5	10	5	5	3	10			
	ρ	1	1	<0·05	—	1	1	0·35			
Cyclohexane	ν	800	992	1028	1268	1445	2853	2890	2921	2937	
	I	4	2	2	2	2	8	2	4	8	
	ρ	0·1	<0·15	0·3	0·4	0·5	0·13	<0·5	0·5	0·1	
Pentane	ν	402	764	843	867	1454	2857	2873	2915	2936	2962
	I	2	1	2	1	3	3	5	3	4	3
	ρ	<0.5	<0.5	<0·5	<0·5	0·3	0·7	0·22	0·7	0·5	0·75

The results with benzene are in fair agreement with those already reported by Cabannes.[2] The case of 1181 is interesting as it happens to show apparently quite different degrees of polarisation according as it is excited by 4046 or 4358; in the former case it is well polarised, the depolarisation being at the most only about 20% whereas in the latter it is almost unpolarised. Such an anomaly arises from the fact that in the former case the well polarised principal line 990 arising from

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Trans. Farad. Soc., 25, 813 (1929).

4077 falls on the top of it and gives it an appearance of a highly polarised line whereas in the latter the line 2946 from 4046 falls on the top of it and gives it the appearance of complete depolarisation. The 990 line is however much more intense than this frequency and it is almost certain that the high polarisation in the former case is largely due to its presence. On the other hand the one corresponding to 2946 is perhaps comparable in intensity with 1181 and the results seem to suggest that both these lines are more or less completely unpolarised. The two close lines at 3046 and 3060 are of special interest as they both arise from hydrogen and are quite differently polarised. The value given by Cabannes differs from either and is midway between the two, a result which may probably be attributed to a superposed effect. The extraordinary intensity of the 990 and 3060 lines and their high degree of polarisation as a contrast to all other lines may be noted.

Polarisation results with cyclohexane and pentane are new and reported here for the first time.

4. *Comparison of the liquids.*

Carbon oscillations.—In the first instance it may be noted that in cyclohexane and pentane most of the Raman lines are well polarised, lines showing large imperfections of polarisation being entirely absent whereas in benzene all lines except 992 and 3060 are more or less completely unpolarised. This outstanding feature of the polarisation of Raman scattering has an analogy in Rayleigh scattering in that the unmodified light scattered by the aliphatic group of compounds shows very little imperfection of polarisation whereas it is largely depolarised in the group of aromatic compounds.

The line of extraordinary prominence in benzene is the one at about 992 which continues to appear in almost all its derivatives in a slightly shifted position, *viz.*, 1000. Remarkable variations in intensity exhibited by this line with increasing complexity of substitution have been discussed in a recent paper by Venkateswaran and Bhagavantam.[3] Its great intensity suggests that it is an inactive oscillation probably corresponding to a symmetric motion of alternate carbon atoms.[4] The curves showing the infra-red absorption of benzene given by Coblentz, Bell and others show only a feeble absorption corresponding to this frequency although there is a prominent absorption maximum in its neighbourhood. The almost complete polarisation of this line is in agreement with such a view and the results already deduced by the author in his previous paper regarding symmetrical oscillations. A study of its polarisation in various derivatives will be of great interest.

When we pass to cyclohexane the line has not changed either in position or in the state of polarisation appreciably, a result which is of great significance as it suggests essentially a similar hexagonal symmetry for the latter molecule also. This is further supported by the fact that as in benzene, this oscillation is inactive in cyclohexane as well and does not give rise to any corresponding absorption in the infra-red region.[5] The only other prominent frequency in cyclohexane, besides those attributable to hydrogen, is the one at 800 and is also not represented by any maximum in the infra-red absorption. This fact as well as its large intensity and polarisation, both suggest that it corresponds to a symmetric distortion of the molecule involving no change in the electric moment. It may be mentioned that both 800 and 992 resemble each other further in that they both are very sharp unlike the other lines in the spectrum. Such a close similarity which the 800 line bears to 992 suggests that both of them probably represent the same oscillation: in the case of 992 carbon atoms alone oscillate whereas a simultaneous disturbance of the attached hydrogen atoms which are more important here than in benzene, will account for the slightly lower value 800 for the second oscillation.

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[3] Proc. Roy. Soc., 128, 252 (1930).

[4] This point is dealt with more fully in another paper by the author.

[5] J. Lecomte, Le Spectre Infrarouge, 217 (1928)

The situation in pentane is however quite different as there exists in the place of this unique oscillation, a series of oscillations 402, 764, 843 and 867 all of comparble intensity and polarisation characters. The chemical analogue of this feature is the distribution of carbon atoms along a zig zag chain in the one case and at the corners of a hexagonal ring in the other.

Hydrogen oscillations.—The lines 1597, 3046, 3060 in benzene; 1445, 2853, 2890, 2921, 2937 in cyclohexane and 1454, 2857, 2873, 2915, 2936, 2962 in pentane have all been attributed to oscillations of the hydrogen atoms by various investigators. It is interesting to note that the intensity and polarisation characters exhibited by this series constitute a very wide range: there are lines of extreme feebleness as well as high intensity and lines showing high degree of polarisation as well as a large imperfection of polarisation. The origin of such a multiplicity of hydrogen frequencies is not clear at present although in a general way it may be connected with the lightness of the atom and the consequent ease with which it is affected by the environment. There is however no explanation which satisfactorily accounts for the observed multi tude of frequencies. It appears reasonable to suppose that the origin of such a multiplicity will also account, if properly located, for the remarkable polarisation and intensity characters. It must however be mentioned here that usually high intensity and large polarisation go together.

In conclusion the author desires to express his best thanks to Prof. Sir C. V. Raman for suggesting the problem and giving valuable help in the course of the work.

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The Origin of the Continuous Spectra in Raman Scattering.

By

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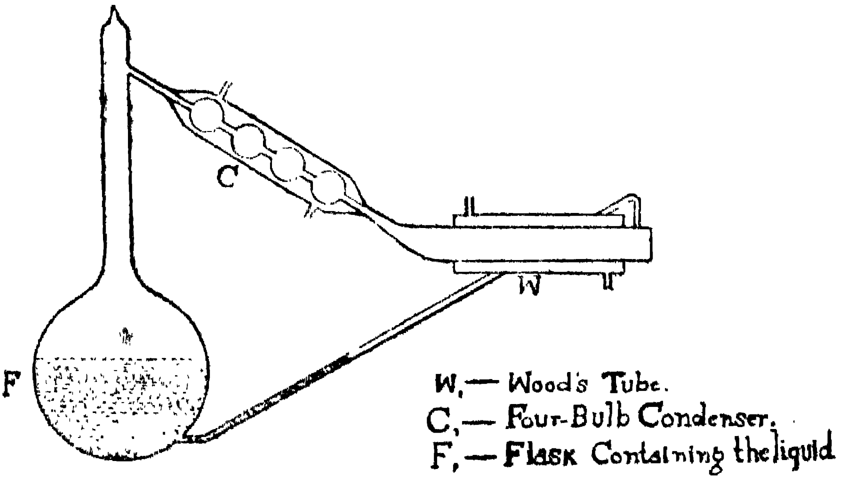
(Plate XXII).

In a recent publication,[1] we have suggested a mechanism of the production of the continuous spectra in the scattering of certain types of organic compounds. In support of our view we will give here a short account of an experiment which has been carried out at Dacca.

Freshly distilled colourless benzaldehyde was taken in an evacuated flask which was connected through a water-cooled condenser to a Wood's tube of the usual pattern, which was further provided with a return tube which again connected it direct to the original flask. Air was carefully avoided by evacuating and a preliminary boiling of the liquid and the apparatus was afterwards sealed off. A diagram of the experimental arrangement is given.



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[1] Ind. Journ. Phys., Vol. V, Part I, 1930.

In a series of exposures, by means of continuous circulation of benzaldehyde, which was kept boiling in an oil-bath, the liquid in the Wood's tube was kept absolutely colourless and the resulting Raman spectrum was obtained (Plate XXII, Fig. a.) The plate was absolutely free from all continuous spectra, the Raman lines appearing in great intensity, which showed clearly the fine structure of the lines, the narrow groups being clearly resolved. The exposure ranged from 1½ to 2 hours.

In another set of exposures we stopped the circulation; the liquid gradually developed a yellow colour, which was noticeable after about fifteen minutes and gradually increased in intensity. The resulting spectrum is given in Plate XXII, Fig. b. The plate used was a soft gradation panchromatic one to find out the extent of the continuous spectrum. The resulting continuous spectrum seems to have a sharp violet edge and extends continuously up to about 6710 A.U.

In benzaldehyde, the first product of photochemical action seems to be a yellow product which seems further to break down under the action of light and thus give rise to the continuous spectrum. Its absence suppresses the continuous spectrum altogether.

We desire to express our best thanks to Prof. S. N. Bose for his kind interest in the work.

Department of Physics,
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The 18th September, 1930.

Fig. a.

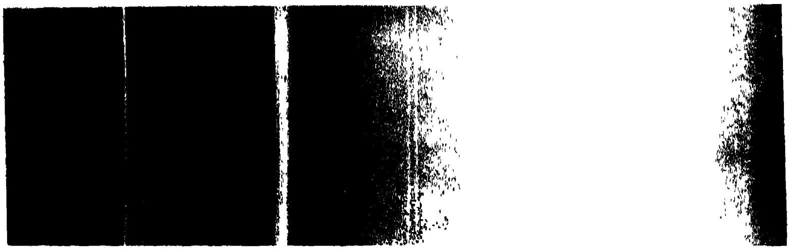

Fig. b.

Fig. a. Raman spectrum of benzaldehyde with constant circulation.

Fig. b. Raman spectrum when the circulation is stopped.

On the Characteristic Frequencies of Radicals in Different Chemical Combinations.

By

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In a previous paper[1] on the Raman effect, we have pointed out how certain characteristic frequencies persist in the various compounds which possess one common radical or a certain type of bond. This fact has been mentioned by other workers and some[2] have even tried to calculate the frequencies from the mass of the constituents and the heat of dissociation. Some[3] have also tried to verify the formula by showing that the effect of increase of mass is in most cases a diminution of the frequency and have seen in this result an analogy with the usual dynamical result of the diminution of frequency with the load.

There is, however, a certain weakness in the argument which has not generally been pointed out. There is the assumption that the strength of the binding between the components of the radical responsible for the oscillation remains the same in all the various compounds. There is actually no experimental data which would justify this assumption and we have therefore thought it worth while to make an intensive study of one radical to clear up this point. We have chosen the CN group: the frequencies to be attributed to CN in the different types of compounds are here collected for reference.

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[1] Ind. Jour. Phys., Vol. V, Part I, 1930.

[2] Dadieu und Kohlrausch, Sitz. Akd. Wien., Vol. 138, p. 419, 1929.

[3] ,, Sitz. Akd. Wien., Vol. 138, pp. 424-428, 1929.

Compounds.	Frequency of CN	Investigators.
Organic :		
$N\equiv C-CH_2COOCH_3$	2266	[5a] Petrikaln & Hochberg.
$N\equiv C-CH_2COOC_2H_5$	2258	[4] Dadieu and Kohlrausch
$CH_3-C\equiv N$	2256	[6] Pal & Sen Gupta
$C_6H_5-CH_2-C\equiv N$	2218	Dadieu & Kohlrausch
$H_5C_2-C\equiv N$	2246	,,
$C_6H_5-C\equiv N$	2227	,,
Inorganic :		
$K-O-C\equiv N$	2183	Pal and Sen Gupta
Complex double cyanides		
$K_2\ Hg\ (C\equiv N)_4$ $K_2\ Zn\ (C\equiv N)_4$ $K_2\ Cd\ (C\equiv N)_4$	2150	Authors
$K\ Cu\ (C\equiv N)_2$ $K\ Ag\ (C\equiv N)_2$	2110	Authors
$K\ C\equiv N$	2080	Pal & Sen Gupta
$Na-S-C\equiv N$	2076	Dadieu & Kohlrausch
$K-S-C\equiv N$	2066	Pal & Sen Gupta
$NH_4-S-C\equiv N$	2066	,,

It will be evident from the consideration of the data, that it is the nature of the bond which plays a predominant part in the determination of the frequency rather than the mass of the substituent radical.

Thus CN linked to an aliphatic carbon, seems to have a characteristic frequency which is but slightly changed by further substitution, in a different position in the chain, as will be at once evident by looking at the table. When, however, CN is linked directly to an aromatic compound, that is to a carbon in the benzene ring the frequency is markedly changed.

[5a] Zeitschr. f. Phys. Chem. Abt. B, 3, 317, 1929; 4, 299, 1929.

[4] Sitz. Akd. Wien., Vol. 139, p. 167, 1930.

[6] Ind. Journ. Phys., Vol. V, Part I, 1930.

A striking series of results have been obtained by the study of the complex metallic cyanides recently carried out by us. It has been found that the frequency remains practically the same when the valency of the complex—forming metal remains the same, so that the complex cyanides formed are of the same type. Here the change of the mass of the substituent seems to have absolutely no effect on the characteristic frequency, which is however at once changed when the valency of the metal is changed, thus:—zinc, cadmium and mercury cyanides have the same frequency, so also the cyanides of silver and copper.

It seems to us that a satisfactory explanation of these facts can be given, on the basis of the electron theory of valencies. The oscillation frequency of the CN radical is determined by the masses of C and N, and by the force of binding, to which both the charges of the nuclei, as well as the electronic configuration surrounding the atoms contribute. When the radical is attached to another atom, it is the electronic configuration surrounding the radical which is affected. According to the degree and strength of the bond, the effect on the electronic ring may vary from an actual increase in the number, due to sharing of electrons with other atoms, to a distortion of the electronic orbits, as will perhaps be evident from the change of the electronic moment, or both. It is then clearly understood how the same type of binding will give rise to the same characteristic frequency and how it will comparatively be unaffected by the mass of the rest of the molecule.

We are seeking for further experimental evidence which will support our ideas and we are studying at present the influence of crystal structure on the frequencies of different radicals like SO_4, NO_3, ClO_3, etc. as well as the influence of the rest of the molecules on the frequencies themselves.

In conclusion the authors express their best thanks to Prof. S. N. Bose for his kind suggestion of the problem and helpful guidance during the progress of the work.

Department of Physics,
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The 18th September, 1930.

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Forms of Oscillation of the Benzene Ring in Raman Effect.

By

S. Bhagavantam.

(*Received for publication, 22nd September, 1930.*)

(Plate XXIII).

Abstract

Utilising the theory of vibrations of an elastic solid circular ring, the geometrical characters of the vibrations of a hexagonal ring have been deduced. Six of them consist of flexural oscillations, three being in the plane of the ring and three perpendicular to it. There are six others all of which involve motion of the nuclei in the plane of the ring only and belong to the extensional type.

Raman frequencies higher than 1500 have been attributed to the oscillations of the hydrogen atoms. The remaining four frequencies at 607, 851, 992 and 1181 are due to the hexagonal carbon ring in benzene. The one at 992 possesses a high intensity and sharpness and is almost completely polarised. It is however represented by only a barely detectable point of inflexion in the infra-red absorption curves. Both these facts suggest that it is an inactive oscillation and it has been identified with a symmetric mode in which all the six carbon atoms move tangentially, three of them situated at alternate corners moving in one phase and the other three in an opposite phase. Such a motion is highly balanced and is very little affected by a loading of the hexagon. In agreement with such an identification, this frequency appears in the Raman spectra of almost all the benzene derivatives, the value remaining practically unchanged. In mesitylene the conditions are very favourable for the presence of this oscillation and it is accordingly very prominent in its Raman spectrum. The frequency at 607 is probably due to the gravest extensional mode in which the hexagon as a whole expands and contracts alternately. 851 and 1181 agree very closely with two prominent infra-red absorption maxima and have been identified with two unsymmetrical modes of the extensional type.

The Raman spectrum is discussed in relation to infra-red absorption. By giving long exposures six new Raman lines of very low intensity at 4163·8, 4397·2, 4438·4, 4494·2, 4505·8 and 4513·0 A.U. have been observed. The first and the fourth are attributed to 4046 and 4358 mercury lines respectively and constitute a new Raman freqnency of 694 agreeing remarkably well with a strong infra-red absorption found by Coblentz at 694 wave numbers. The two lines at 4397·2 and 4438·4 are attributed to 4046, their frequency shifts corresponding to 1970 and 2181 wave numbers. The former agrees closely with a sharp and prominent infra-red absorption observed both by Bell and Daugherty. The origin of the two lines at 4505.8 and 4513·0 is not decided although infra-red absorption data suggest that they arise out of 4358. Taking the observed Raman frequencies as fundamentals, all the infra-red absorption frequencies higher than 1100 which are unrepresented in the Raman spectrum are successfully explained as due to simple combinations.

1. *The oscillations of a hexagonal ring.*

The modes of vibration of an elastic solid in the form of a complete circular ring[1] were experimentally studied by Chladni and their theory has been investigated by Hoppe, Michell and Basset. They fall into three classes, namely the flexural, extensional and torsional respectively. Unless the ring is exceptionally thick its torsional or extensional vibrations are of a much higher frequency than the flexural or transverse oscillations. The latter class may be either in the plane of the ring or perpendicular to it ; in either case the frequencies do not differ appreciably and during the oscillation the ring divides up into 4, 6, 8 or larger even number of vibrating segments. We need not stop to consider the torsional modes of vibration, but will pass on to deal with those of the extensional type. It must be remarked that these involve displacements both tangential and radial to the ring. The radial displacements are as important as the tangential in the first few modes but become negligible in the higher modes which approximate in character to the longitudinal vibrations of a straight rod. The expressions for the displacements are u (radial) $=(A \sin n\theta + B \cos n\theta) \cos(pt+\epsilon)$ ω (tangential) $= n(A \cos n\theta — B \sin n\theta) \cos(pt+\epsilon)$ where p^2 varies as $(1+n^2)$.

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[1] Theory of Elasticity by Love, 3rd Edition, Chapter XXI

When $n=o$, we have the simplest mode in which the ring expands and contracts symmetrically, remaining circular in form. For the modes $n=o$, $n=1$, $n=2$ and $n=3$ the displacements are as shown in fig. 1.

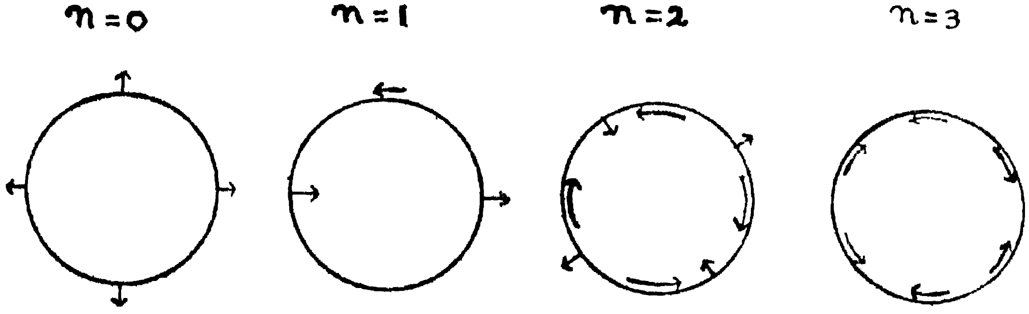

Fig. 1. Extensional oscillations of a circular ring.

We may now imagine the circular ring to be loaded equally at points along the circle sixty degrees apart. If the loads be sufficiently increased, and if at the same time, we imagine the elasticity of the wire increased in proportion, we ultimately pass over into the case of the hexagonal ring of six particles elastically connected with each other and capable of oscillation. In the process of loading the ring, both its frequencies and modes of vibration will naturally be altered. We may however obtain a hint as to the behaviour of the system in the final case by considering the initial effects of loading on the oscillations of a circular wire. When small equal loads are fixed at opposite ends of a diameter, their effect on the frequency depends on their position with reference to the form of oscillation. In general, each mode of oscillation would bifurcate into two, one of lower frequency involving a maximum oscillation at the points of fixation of the loads and another in which the alteration of frequency is smaller or negligible. It is obvious that in the limiting case when the loads are very great in comparison with the mass of the wire, we are chiefly concerned with the vibrations of the first kind. It is further evident that we are only concerned with modes of oscillation having three or fewer nodal diameters.

Utilising these principles, the following may be inferred as possible modes of vibration of a hexagonal ring. The three cases in fig. 2 represent flexural oscillations in the plane and those in fig. 3 represent flexural oscillations normal to the plane of the ring respectively. In the latter case the plus and minus

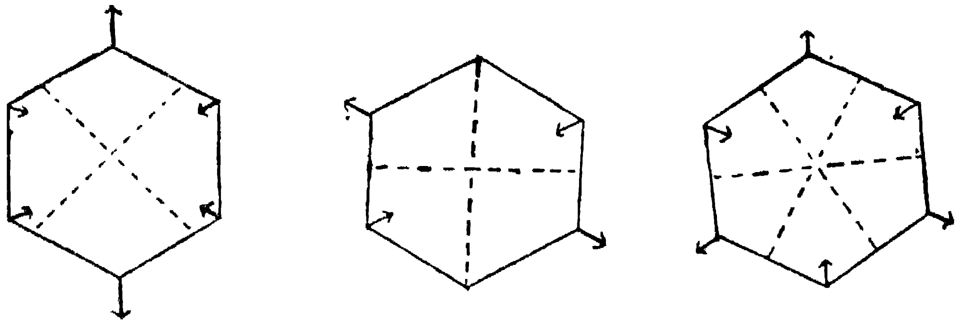

Fig. 2. Flexural oscillations in the plane.

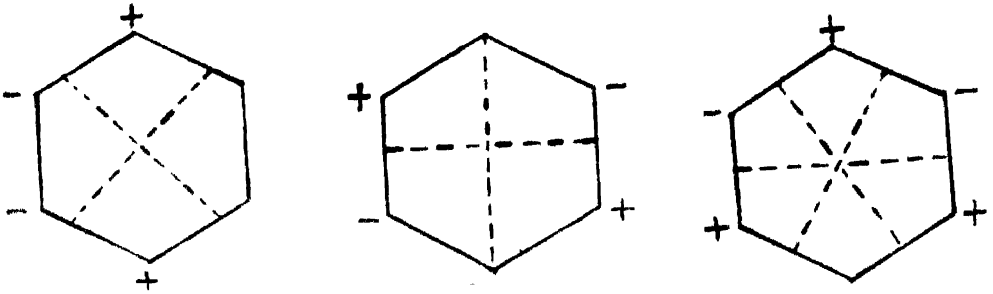

Fig. 3. Flexural oscillations perpendicular to the plane.

signs indicate motion upwards and downwards respectively from the mean plane of the hexagon. Fig. 4 on the other hand contains six modes all of which are of the extensional type.

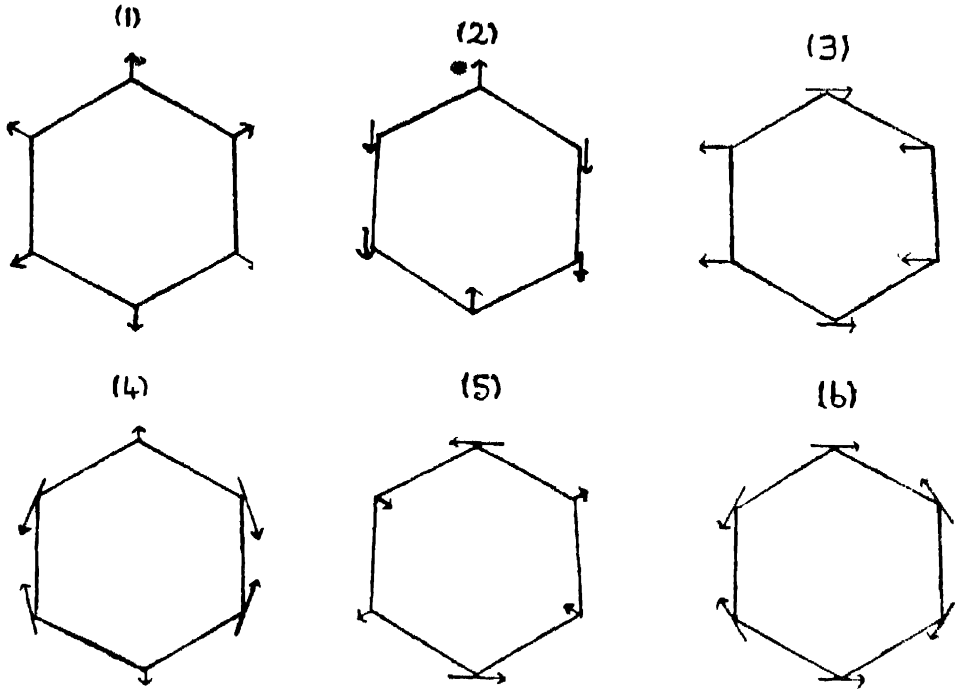

Fig. 4. Extensional oscillations.

2. *The Raman spectrum of benzene.*

Frequencies 607, 851, 992, 1181, 1586, 1608, 2948, 3046, 3063, 3168 and 3185 have been found in the Raman spectrum of benzene by various investigators. The higher frequencies ranging from 2948 to 3185 have been attributed to hydrogen oscillations in view of its relatively low atomic weight. Amongst these, the most conspicuous in intensity is 3063: it is also strongly polarised. 3046 is less intense and much less perfectly polarised. The doublet with frequencies at 1586 and 1608 may also be ascribed on the following grounds to an oscillation specially involving the hydrogen atom. The aliphatic hydrocarbons show a series of frequencies somewhat lower than in the aromatic compounds ranging from about 2850 to 2960 which are attributed to oscillations of the hydrogen atoms. In addition to these, a frequency of about 1450 is also present in all aliphatic compounds containing hydrogen.

That this has also its origin in the hydrogen atoms may be seen by comparing the Raman spectra of carbon tetrachloride and chloroform. The latter compound shows two frequencies 1440 and 3020 which are both absent in the former. The view that this lower frequency represents an oscillation in the direction transverse to the chemical bond has been expressed by Ellis[2] and others. Extending the analogy to the aromatic hydrocarbons, it appears reasonable to likewise associate the doublet at 1586 and 1608 with a transverse oscillation of the hydrogen atom.

The four other frequencies 607, 851, 992 and 1181 have evidently to be associated with the oscillations of the carbon atoms. The Raman lines corresponding to these frequency shifts show great differences in their intensity, sharpness and degree of polarisation. The 992 Raman line is many times more intense than the others. It is also extremely sharp, in fact as sharp as the exciting mercury line. It exhibits a very nearly complete polarisation while the other three lines are very imperfectly polarised. Next to the 992 oscillation, the most intense one is that at 607 while the two others at 851 and 1181 are of comparable intensities. These remarkable differences in their characters constitute a strong evidence in support of the view that they are all independent frequencies representing the various modes of oscillation of the benzene ring composed of six carbon atoms. The Raman frequencies will now be individually discussed with a view to identify them with one or other of the normal modes deduced for a hexagon in the foregoing section.

3. *The origin of the Raman line 992.*

From the general characters of the Raman spectrum of benzene described in the foregoing section, it is evident that the oscillation at 992 is on an altogether different footing from the rest. Its importance may be realised from the fact that it appears in the Raman spectra of almost all the benzene derivatives, the value remaining practically unchanged. This result is very significant as it suggests that the mode of oscillation which it represents is so balanced that a loading of the benzene ring has no effect on it. It appears as a prominent vibration frequency in the ultra-violet absorption of various aromatic compounds containing the benzene nucleus[3]. In the excited molecule however, the frequency undergoes a considerable alteration which varies from compound to compound. It also plays an important role in the fluorescence spectrum of benzene[4]. The recent investigations of Kronenberger[5] show that it appears in the luminiscence spectra of benzene and its derivatives examined at low temperatures.

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[2]. Jour. Frank. Inst., 208, 517(1929).

It is a matter of experience that in the Raman effect those oscillations which involve no alteration of the electric moment of the molecule appear with great intensity[6]. Such oscillations are said to be optically inactive as they are incapable of causing direct absorption by themselves in the infra-red region. The well known cases of CO_2, CS_2, CO_3, and NO_3 may be cited as examples. The principal Raman lines in all these cases represent optically inactive oscillations and are very intense and sharp. The great intensity and sharpness of the 992 line in benzene suggests a close similarity to all the above cases and may on the strength of analogy be taken as evidence that it represents a symmetric mode of oscillation in the molecule.

This view is strongly supported by the evidence from infra-red absorption. In the absorption curves for benzene liquid given by Coblentz[7] and by Bell[8] the frequency 992 is represented only by a barely detectable point of inflexion. If the 992 frequency were that of a strictly inactive oscillation, we should expect to find no trace of it in the absorption curve. On the other hand its weak presence in the infra-red absorption is perhaps suggestive of a slight departure from perfect hexagonal symmetry in the benzene ring. Such a result has been contemplated by various authors amongst whom special reference may be made to the recent work of Mrs. Lonsdale [9] on the structure of hexamethylbenzene. An alternative explanation may be found in the fact that the absorption has been studied in the liquid state where the interaction of the neighbouring molecules is of importance and might result in a very slight distortion of the hexagonal structure. If the latter view is correct, one might venture to suggest that this weak absorption would altogether disappear in the vapour state. From this point of view a study of the Raman effect and infrared absorption of benzene in the vapour state will be of great interest.

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[3] R. Mecke, Handbuch d. Physik, 21, 552 (1929).

[4] C. V. Shapiro, Nature, 124, 372 (1929).

[5] Zeit. f Phys., 63, 437 (1930).

[6] A simple explanation has been suggested by C. Ramaswamy, Ind. Jour. Phys, 5, 193 (1930).

[7] Investigations of Infra-red spectra, Carnegie Inst., (1905).

[8] Jour. Amer. Chem. Soc., 47, 2811 (1925).

It must be stated that in the close vicinity of this oscillation there appears a strong infra-red absorption at 1030 wave numbers which is not represented at all in the Raman spectrum of benzene. This has hitherto been identified with the 992 line, a view which is evidently wrong as the discrepancy is far too great to be due to experimental errors. On the other hand, there is considerable evidence suggesting that 1030 is very characteristic of the benzene ring as it appears in the Raman spectra of all benzene derivatives and is as prominent as 992 itself in some cases. Considerable variations are observed in the relative intensities of these two lines from compound to compound. In benzene itself 992 alone appears with great intensity ; in the mono-derivatives it is slightly weakened but still stronger than 1030 ; in the di-derivatives they are of comparable intensities whereas in the one case of a symmetrically substituted tri-derivative studied so far viz. mesitylene, the line 992 regains its original inintensity and is many times stronger than 1030 which is very weak, a state of affairs very much like that in benzene. In cyclohexane, on the other hand, both of them appear with comparable intensity. The significance of such a strong infra-absorption at 1030 in benzene with no corresponding line in its Raman spectrum and its relation to the principal 992 line are not clear.

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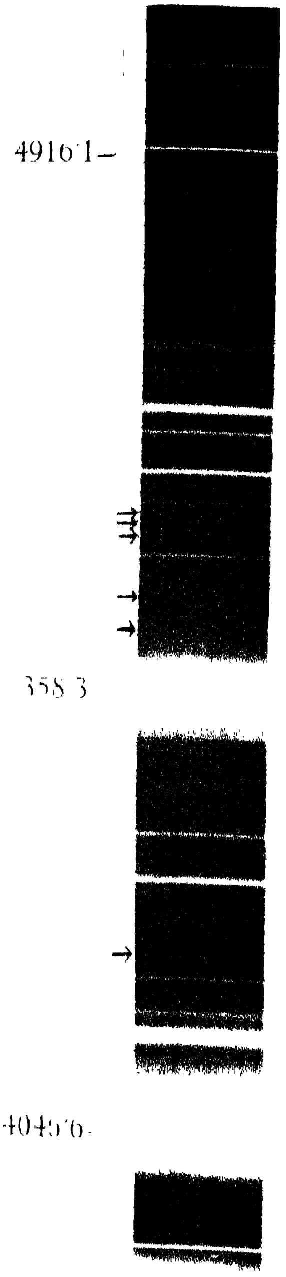
[9] Proc. Roy. Soc., 123, 494 (1929).

There is however little doubt that 992 is a symmetric oscillation of the benzene ring and hence can be identified with case 6 in fig. 4. All the six particles undergo tangential displacements, radial motion being unimportant. Such an identification at once explains many of the above noted experimental facts. In the first instance it will be optically inactive and cannot be observed in the infra-red absorption. As the motion is tangential, the effect of loading the ring at the ends of radially directed chemical bonds will be unimportant ; the situation would have been quite different if the motion were radial. The oscillation has three nodal diameters and possesses a trigonal symmetry in agreement with its extraordinary intensity in mesitylene. Finally it must be mentioned that any slight asymmetry of the ring, which may be a temporary one due to environment or a permanent one due to an inherent nature of the benzene molecule itself, will also be shared by the oscillation and it begins to appear in the infra-red absorption. Variations of intensity in the Raman spectra of the benzene derivatives may also be due to such an effect of unsymmetrical loading on this oscillation.

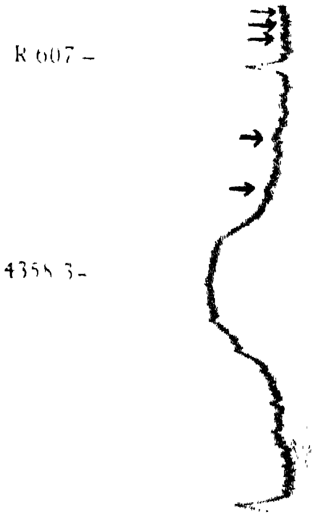
4. *Some general considerations.*

The theory of the vibrations of an elastic solid ring has been used in the foregoing section to obtain an indication of the geometrical characters of the vibration which the hexagonal ring in benzene is capable of. We must notice however that no numerical correspondence can be expected between the two cases as regards the frequencies of the different modes and indeed even the sequence in which these frequencies are arranged may be quite different. This is because, in the first instance, the distribution of masses in the benzene ring is very different from the uniform distribution assumed for a circular ring. A more important point is that there may be no justification for assuming that the nature of forces in the molecules is even approximately of the same type as in flexure or extension of an elastic solid. We have as yet but little knowledge as to the nature of the forces within the molecule which determine its frequencies of oscillation. The atoms in the carbon ring are held together by homopolar bindings, the forces due to which are known to diminish rapidly with increasing distance between neighbouring atoms. We may picture the forces to be of three different kinds, acting between carbon atoms situated with respect to each other in the ortho, meta and para positions, and these are presumably of very different magnitudes. The influence of these three classes of forces on the frequencies of the different modes of vibration will obviously be very different in different cases. Those frequencies which involve large radial displacements of the nuclei will be affected most by para forces, to a lesser extent by the meta forces and still less by the ortho ones. On the other hand, oscillation frequencies in which the tangential displacements are more important will be influenced by the existence of para forces to only a negligible extent. That the frequencies for different forms of vibration of the benzene molecule do not follow the same order as for the case of an elastic ring is evident from the fact that we have been forced by the logic of facts to identify the 992 Raman line with a six-nodal oscillation of the extensional type ; in the case of the elastic ring this would be the mode having the highest frequency whereas in benzene, we have at least one frequency of the carbon ring viz., 1181 which is higher.

It will be seen from the diagrams given in figs 2 and 4, that some of the modes of the extensional type are very similar to those of the flexural type in the plane of the ring, and it is possible that in the benzene molecule they become indistinguishable. Even allowing for such coincidences, the



Raman spectrum of benzene.



Microphotometer record

number of modes of vibration to which frequencies have to be assigned is much greater than the number of Raman lines hitherto recognised. This indicates that the Raman lines corresponding to several of the possible modes of vibration have either been overlooked in the investigations so far published owing to their low intensity or other causes, or that for some unknown reason they fail to appear in the spectrum of the scattered light. Until the full number of Raman lines are experimentally observed, the recognition of the various possible modes of vibration and the assignment of the frequencies to them must remain somewhat hypothetical. We may however endeavour to settle the matter as far as possible by studying critically the relation of the Raman spectrum to the infra-red absorption curves of benzene, and the variations of both, consequent on different chemical substitutions in the benzene molecule.

5. *Relation to infra-red absorption.*

The infra-red absorption of benzene liquid has been studied by Coblentz in the region 1 to 15 μ, by Bell from 1 to 12 μ and by Daugherty [10] from 1 to 7μ and more recently by Barnes [11] from 3 to 3·6 μ. The results given by these authors have been carefully examined with a view to arrive at a proper interpretation of the Raman spectrum and its relation to infra-red absorption. A remarkable feature noted by Coblentz in the long wave length region is that there is a very complete absorption whose maximum corresponds to about 694 wave numbers which lies just within the limit to which his investigation was extended. That this is a genuine absorption characteristic of benzene is clear when we see his curves for other liquids such as the xylenes which do not show any marked absorption in this region. In the entire range investigated by the above authors, this band stands out as the most prominent one. Surprisingly however,

[10] **Phys. Rev., 34, 1549 (1929).**

[11] **Phys. Rev., 35, 1524 (1930).**

the corresponding frequency has not hitherto been observed in the Raman spectrum of benzene. Such a low frequency cannot be explained as a combinational one and has certainly to be regarded as one of the fundamental frequencies characteristic of the benzene molecule. Its high intensity of absorption suggests that it is a strongly active oscillation and may perhaps be very weakly present in the Raman spectrum, contrary to the case of inactive oscillations. That such is actually the case may be seen from the results described in the next section. Long exposures have revealed the existence of a frequency having precisely the same value in the Raman spectra as well and hence there is little doubt that it represents one of the fundamental frequencies. The next strong absorption is at 772 and is not represented in the Raman spectrum. There are however, two weak lines observed by the author at 4505·8 and 4513·0 A. U. which if attributed to the 4358 mercury line, will have frequencies 751 and 788 respectively which are in the close neighbourhood of the infra-red value 772. The assignment is however uncertain at present and the existence of such a frequency can only be tentatively assumed. Such an assumption explains almost all the infra-red absorption data as may be seen from Table 1, in view of which the frequency may perhaps be taken as a real fundamental.

The next strong absorption at 847 wave numbers coincides very exactly with the weak Raman frequency 851 and is also presumably an assymmetric fundamental oscillation. It has already been remarked that corresponding to 992 there is only a weak point of inflexion following which a strong absorption at 1024 occurs which is not represented in the Raman spectrum. 1183 is the next strong one and is in excellent agreement with 1181 as revealed in the Raman spectrum. The value of this frequency is taken from Bell's curve and is in slight disagreement with that of Coblentz. After this, there follows a series of absorption maxima at 1316, 1380, 1486, 1587, 1613, 1818, 1968 etc. wave numbers extending well into the short wave region, some being intense and others feeble but definite. It is reasonable to suppose that most of these represent combinational frequencies, although some of them being in the high frequency region may be attributed to the primary oscillations of the hydrogen atom. Of these the one at 1968 needs special mention. It has not been reported by Coblentz but can be seen as a remarkably sharp and prominent absorption in the curve given by Bell and agrees very well with one of the Raman frequencies viz., 1970, as shown below. The following table shows the relation between the Raman spectrum and infra-red absorption. The infra-red data are collected from the various authors quoted above and the best representative values given.

TABLE I.

Raman frequencies.	Infra-red observed.	Calculated	Assignment.	Raman frequencies.	Infra-red observed.	Calculated.	Assignment.
ν_1 : 607 (*s*)							
ν_2 : 694 (*f*)	694 (*s*)	—		ν_8 : 1608 (*f*)	1613 (*f*)	—	
ν_3 :	772 (*s*)	—			1818 (*s*)	1843	$\nu_4+\nu_5$
	803 (*f*)	—		ν_9 : 1970 (*f*)	1968 (*s*)	—	
	820 (*f*)	—			2040 (*f*)	2032	$\nu_4+\nu_6$
				ν_{10} : 2181 (*f*)			
ν_4 : 851 (*f*)	847 (*s*)	—			2269 (*f*)	2280	$\nu_2+\nu_7$
ν_5 : 992 (*s*)	985 (*f*)	—			2326 (*f*)	2302	$\nu_2+\nu_8$
	1024 (*s*)	—			2667 (*f*)	2664	$\nu_2+\nu_9$
ν_6 : 1181 (*f*)	1183 (*s*)	—			2856 (*f*)	2821	$\nu_4+\nu_9$
					2894 (*f*)	2875	$\nu_2+\nu_{10}$
	1316 (*f*)	1301	$\nu_1+\nu_2$	2948 (*f*)			
				3046 (*f*)	3040 (*s*)	—	
	1380 (*s*)	1379	$\nu_1+\nu_3$				
				3063 (*s*)	3074 (*s*)	—	
	1486 (*s*)	1466	$\nu_2+\nu_3$				
					3095 (*s*)	—	
ν_7 : 1586 (*f*)	1587 (*f*)	—		3168 (*f*)			
				3186 (*f*)			

It will be seen that in most cases, although there is a reversal in intensities, the Raman frequencies agree remarkably well with the observed infra-red values. All the absorption bands lying beyond 1024 and which do not coincide with any of the observed Raman frequencies have been explained as due to simple combinations of them. A strong absorption at 772 is not represented in the Raman spectrum but is taken as a fundamental. It may be noted that 694 which is the strongest in infra-red absorption and just detectable in Raman spectra occurs a large number of times in the combinations. Many of the discrepancies noted hitherto regarding the relationship between Raman and infra-red spectra may be due to the fact that such weak lines have been overlooked in the Raman spectra.

The very exact coincidence of the two faint Raman frequencies ν_4 and ν_6 with two strong infra-red absorption maxima suggests that they are optically active oscillations and may perhaps be identified with cases 2 and 3 respectively in fig. 4. Such an identification is strongly supported by the following considerations. If a load is placed at any one corner of the hexagon the existence of these two modes becomes very improbable. In the mono-substituted derivatives such an unsymmetrical loading takes place, examples of which are toluene, ethylbenzene etc. In these compounds ν_4 and ν_6 are either entirely absent or much weaker than in benzene.[12] On the other hand loading of the hexagon may take place at two corners in which case various possibilities have to be considered. In case the corners for loading are chosen as the ortho or the meta positions the ring is rendered unsymmetrical and the oscillations become much less probable. Simple examples in practice are to be found in the set of xylenes. In ortho and meta-xylenes the two frequencies are again either absent or very weak. The para-xylene stands on a different basis and the substitution may take place at corners where either nearly tangential or nearly radial motion alone exists. In the former case the frequencies should be practically unaffected, whereas in the latter they are likely to be slowed down. Accordingly the Raman spectrum of para-xylene is quite different from those of ortho and meta-xylenes in that there are two strong frequencies 828 and 1208 in the neighbourhood of ν_4 and ν_6. The existence of some lower frequencies also which are slightly more prominent than in the other two xylenes is significant.

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[12] The experimental evidence quoted here is mostly taken from A. S. Ganesan and S. Venkateswaran, Ind. Jour. Phys., 4, 195 (1929).

The origin of 607 and 694 is not clear. The latter is a strongly active oscillation and must represent a very unsymmetrical mode. The intensity of the former on the other hand comes next to the 992 line and there is a likelihood of its being inactive in which case it may be taken to correspond with the lowest extensional mode in which the hexagon as a whole expands and contracts (case 1 in fig. 4). There is no clear evidence either in support of or against this view. Infra-red investigations have not been carried so far.

6. *A search for other frequencies.*

It will be seen that oscillations of the flexural type lying in the plane as well as those that are perpendicular to it have not been dealt with and all the observed ones have been identified with oscillations of the extensional type. The existence of additional oscillations of the above type is however clearly implied in the theory and it is therefore thought that an experimental search ought to be made to detect any frequencies in benzene which may possibly have been overlooked hitherto.

A long wide tube containing Kahlbaum's benzene purified by redistillation in vacuum is used. The liquid is illuminated by focussing on it the light of a mercury arc lamp by means of a powerful condenser. The scattered light is photographed with a large two prism glass spectrograph supplied by Adam Hilger. With the above manner of illumination, direct light is very completely eliminated and a long exposure (48 hrs.) given. Table II contains the frequencies of benzene which have already been observed by various authors. The mean results given in column 1 of the Table are mostly accurate to within one wave number.

TABLE II.

Exciting line / Mean frequency	3650·1	3651·8	3663·3	4046·6	4077·8	4339·2	4347·5	4358·3
607				607	607			607
851				851				852
992				992	993	995	992	±992
1181				1182	1183			1179
1586				1586			1584	1585
1608				1608			1608	1607
2948	2950	2948		2946	2947			2950
3046			3048	3047	3046			3046
3063	3064	3062	3063	3063	3059		3059	3063
3168	3162	3166		3168	3163			
3186	3186	3186		3185	3185			

Besides these frequencies six other Raman lines at 4163·8, 4397·2, 4438·4, 4494·2, 4505·8 and 4513·0 A.U. have been observed by the author. In the enlargement and the microphotometer record reproduced in Plate XXIII, these lines are marked by arrows. The reality of their existence has also been verified by re-examining two earlier photographs of benzene scattering obtained by Ganesan and Venkateswaran in this laboratory. The two lines at 4163·8 and 4494·2 are each shifted by 695 and 693 wave numbers from 4046 and 4358 lines respectively and are evidently to be assigned in that manner. This frequency is very weak and its relation to the strong infra-red absorption at 14·1μ observed by Coblentz has been dealt with in the foregoing section. The two lines at 4397·2 and 4438·4 have been independently obtained by Dabadghao in this laboratory and reported elsewhere.[13] They have been conjecturally assigned by him to 4046. The same view is adopted here on the follow-

[13] Ind. Jour. Phys., 5, 207 (1930).

ing grounds. The one at 4397·2 is shifted by 1970 wave numbers from 4046 and concides very exactly with a sharp infra-red absorption band of benzene observed by Bell. A lantern slide made from a photograph of the scattered spectrum of benzene taken by Prof. Raman and K. S. Krishnan in this laboratory with the excitation of 4358 line alone has been examined. The line corresponding to a shift of 694 wave numbers could be seen but neither the line at 4397·2 nor the one at 4438·4 is present although one of them is much stronger. As regards the two other lines at 4505·8 and 4513·0, their origin is very uncertain and can only be decided after further experimentation. The infra-red absorption data seem to favour the view that they come from 4358. On the other hand if they are to be attributed to 4046 the frequency shifts will presumably represent the hydrogen oscillations and afford a most interesting series bridging the hitherto vacant gap ranging from about 1600 to 2800 wave numbers. The existence of all the above six lines is however quite certain although the origin of two of them has not been definitely located.

In conclusion the author desires to express his best thanks to Prof. Sir C. V. Raman for giving many helpful suggestions in the course of the work.

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Raman Spectra of Inorganic Crystals: Part I.

Substances containing XO_3 and XO_4 Groups.

By

P. Krishnamurti.

(Plate XXIV).

(*Received for publication, 20th September, 1930*).

Abstract.

Raman spectra of some inorganic substances containing XO_3 and XO_4 groups have been examined by the powder method. A number of suitably designed pyrex mercury arcs have now been used for intense excitation.

The principal frequency of the *chlorates* ($\nu_3 = 930$ cm.$^{-1}$) becomes smaller with *bromates* and *iodates*, but splits up into two components in $NaBrO_3$ (770, strong and 842, weak), and into four components in KIO_3 (733, 751 strong; 784, 808 weak). In the chlorates, all the frequencies observed are active ones, since there are corresponding infra-red maxima. This is due to the halogen atom lying outside the plane of the oxygen atoms, in agreement with X-ray evidence. The splitting up of the line in the bromates and iodates is discussed in relation to the structure of the groups.

The *intensity* of scattering increases from the chlorate to the bromate, and is exceptionally strong in the iodate. An explanation for this phenomenon is offered on the basis of the electronic theory of valency.

Aqueous solutions of the chlorates give Raman lines in the same positions as in the crystal. But the components of the principal frequency tend to disappear in the solutions. A similar remark applies also to the bromates and iodates.

Among substances with XO_4 group, sodium and ammonium *perchlorates* give Raman lines ($\nu_1 = 462$; $\nu_2 = 633$; $\nu_3 = 933$ cm.$^{-1}$) quite similar to those of the sulphates. Potassium *periodate* gives two lines which could be identified as ν_3 (794, strong; 841, weak). The ClO_4 frequencies do not show any appreciable change on solution, but those of the IO_4 change considerably.

Ammonium molybdate gives comparatively intense Raman lines. A doubling of the principal frequency is observed (932, strong ; 880, medium) which can also be seen is solution. *Sodium tungstate* gives only one line (928 cm.$^{-1}$) which is unaltered on solution. These two substances do not show the expected shift of the principal line towards shorter wavelengths with increasing weight of the central atom.

1. *Introduction.*

It will be realised that an accurate comparison between the Raman spectra and infra-red absorption in simple types of substances, especially when correlated with independent X-ray evidence, will enable an exact determination of the grouping of the atoms and their characteristic oscillation frequencies. Such simple cases occur frequently in the domain of inorganic chemistry where particular groupings of atoms or 'radicals' as they are often called, preserve their entity whether in the solid state or in solution, whose reactions form the main basis of analytical chemistry. As typical examples of simple groups could be cited CO_3, NO_3, ClO_3, BrO_3, IO_3, SO_4, MnO_4, CrO_4 and ClO_4; OH, CN, CNS, CNO, besides various other complex radicals like the pyro—and persulphates or the nitro-prussides. It was recognised by Prof. Clemens Schaefer that such groups could be characterised not only by their chemical reactions but also by their infra-red absorption or reflection maxima. He therefore carried out extensive investigations on the sulphates, carbonates, nitrates, sulphates, chromates, halogenates and silicates, and in each case found that particular frequencies could be attributed to the anion which are influenced only to a small extent by the cation. However, the inactive frequencies or those which do not produce any change in the electric moment of the group do not appear in infra-red absorption, and hence the discovery of the Raman effect where such inactive frequencies appear strongly enables an exact computation of all the fundamental frequencies of simple atomic groups.

Among inorganic substances with simple radicals, the carbonates, nitrates and sulphates have till now been extensively studied both in the solid state and in solution, and the results compared with the infra-red reflection data of Schaefer and his pupils. X-ray investigations showed that the CO_3 or NO_3 ion could be pictured as a plane equilateral triangle with the N atom at the centre and the oxygens at the corners. The four fundamental frequencies characteristic of such a grouping have now been established both by the Raman and infra-red methods. Similarly, the SO_4 ion could be pictured as a regular tetrahedron with the S atom in the centre and the oxygens occupying the four corners. Such a system has been shown to have four frequencies, two active and two inactive. The former have been recorded by Schaefer in the infra-red, while all the four have been observed in the Raman spectra both of crystals and of solutions.

So far, definite models have been assumed for the different groups and the Raman lines explained on the basis of such a model. But it will be seen that in practice any ion does not exist in free space, but is surrounded by other atoms with varying fields of force. This influence could be best judged from the positions and intensities of the Raman lines themselves in different substances containing the same group. Since single crystals of many substances are not usually available for investigation, the powder method first suggested by Menzies and Bar has been applied to this problem by the present author with improved technique. Numerous nitrates, chlorides and sulphates have been so far examined with special reference to the positions and intensities of the inactive frequencies which show changes from crystal to crystal.[1] This has now been extended to a series of chlorates, bromates and iodates which contain the XO_3 group where X is the halogen atom, and to some perchlorates, periodates, molybdate and tungstate, which contain the XO_4 group. The substances have all been examined as coarse crystals or crystalline aggregates, and attempts have been made to correlate the results with the Raman spectra of their solutions, infra-red reflection data of the crystals, and with the structure of the groups as determined by X-ray analysis.

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[1] Krishnamurti, Ind. J. Phys., 5, 1, 113, 183(1930).

2. *Experimental Technique.*

The arrangements were similar to those described in the previous investigations. The substance which was of Merck's or Kahlbaum's origin was placed in a small triangular glass cell, (the two walls inclined to each other at about 120°), illuminated from the top, and the scattered light from the side focussed on the slit by a system of two lenses. A Fuess glass spectrograph with a Rutherford prism gave a large dispersion (about 20A per mm. at 4300A) and good resolution. Special mercury arcs were were constructed in this laboratory for this work, which were made of narrow pyrex tubing, sealed at the ends with tungsten wires. The ends were so designed that two or more lamps could be placed close together giving intense illumination. A current of about 4 amps. was sent through the lamps connected in series, and cooled by a vigorous blast of air from a fan. If this were not done, the lamp usually punctures due to the intense heat developed. The intensity was so great that even working with fine slits and with fine powders, a good spectrogram could be obtained in an hour or two. A concentrated solution of didymium chloride was used as a filter for some substances, which served to bring out faint Raman lines close to the incident line (4358A).

3. *Results.*

The substances examined fall into two groups, firstly those of the XO_3 type which include sodium, potassium, and barium chlorates; sodium and potassium bromates ; potassium iodate and iodic acid ; secondly those of XO_4 type which consist of sodium and ammonium perchlorates, potassium periodate, ammonium molybdate and sodium tungstate.

The exciting lines were the 4046 and 4358 of the mercury arc, and only the Raman lines excited by the latter were accurately measured by comparison with iron arc spectrum taken on the same plate. The lines excited by the 4046 were useful in confirming the assignment. The results for the XO_3 group are set forth in the following table :—

TABLE I.

Chlorates, Bromates and Iodates.

(Exciting line, 4358·34 I.A., $\nu=22938 \cdot 1$).

Substance.	Wavelength in I.A.	ν	$\Delta\nu$ (cm^{-1})	λ in μ	Intensity	λ Infra-red in μ	Remarks.
Sodium Chlorate $NaClO_3$	4451·8	22457	481	20·8	Faint	25·0, 16·04	Merck. Cubic system.
	4542·82	22006·6	931·5	10·74*	Strong	10·04	
Potassium Chlorate $KClO_3$.	4452	22456	482	20·7	Faint	16·22	Merck. Monoclinic
	4543·45	22003·3	934·8	10·70	Med. str.	10·12	
	4551	21967	971	10·30*	Faint		
Barium Chlorate $Ba(ClO_3)_2 \cdot H_2O$.	4454·4	22443	495	20·2	Faint	19·6	Merck. Monoclinic prismatic
	4479	22320	618	16·2	V. faint, br.		
	4539·10	22024·6	913·5	10·95	Med. str.		
	4542·51	22008·2	929·9	10·75	Strong	10·24	
Sodium Bromate $NaBrO_3$	4430	22567	371	27·0	Faint, br.	23·0	Merck. Cubic
	4515·21	22141·2	769·9	12·55	Strong	12·24	
	4524·44	22096	842	11·88	Faint		

* Two faint companions visible.

Substance.	Wavelength in I.A.	ν	$\Delta\nu$ (cm^{-1})	λ in μ	Intensity.	λ Infra-red in μ	Remarks.
Potassium Bromate K BrO_3	4427·3	22581	357	28·0	Faint		Merck.
	4511·44	22159·7	778·4	12·85	Med. str.		
	4513·86	22147·8	790·3	12·65	Strong		
	4522·74	22104·3	833·8	11·99	V. faint		
Potassium Iodate** KIO_3	4502·10	22215·6	732·5	13·65	Strong		Merck.
	4505·94	22186·7	751·4	13·31	V. Strong	13·16	
	4512·63	22153·8	784·3	12·75	Med. str. br		
	4517·39	22130·5	807·6	12·38	,,	12·48	
Iodic Acid HIO_3	4421·4	22611	327	30·6	Med. str.		
	4482·0	22305	633	15·8	Strong		
	4498·07	22225·5	712·6	14·03	Strong, br.		
	4511·89	22157·4	780·7	12·81	Strong.		

** Two very faint lines at about 4416 and 4423A.

It should be remarked here that the bromates gave stronger lines than the chlorates even though the latter consisted of better crystals. The iodates gave the strongest lines of all, in spite of the fact that the crystalline aggregates were almost opaque. In fact, the anti-stokes component of the principal IO_3 lines (13·31 and 13·65μ) appeared with medium intensity in spite of the large frequency shift. Among the XO_4 groups, the molybdate showed remarkably strong lines. The significance of these results will be discussed in a later section.

4. *Chlorates, Bromates and Iodates.*

Relation to crystal structure :—In the case of the carbonates and nitrates which also contain the XO_3 group, an inactive frequency had to be postulated to explain all the infra-red absorption bands. In the case of the chlorates, bromates and iodates considered here, there is no necessity to postulate any inactive frequency since all the infra-red maxima find a counterpart in Raman spectra, and hence are all active frequencies. Hence we have to assume that the central halogen atom does not lie in the plane of the oxygen atoms, but outside it. This is supported in a remarkable way by X-ray data in the case of sodium and potassium chlorates. The former is a typical case since it crystallises in the cubic system. Zachariasen[2] has shown from absolute intensity measurements that the ClO_3 group has an independent existence in the lattice, the three oxygens forming an equilateral triangle, the chlorine atom lying at a distance of 0·48 A from this plane, the distance of O—O being 2·376 A and Cl—O, 1·476 A. $KClO_3$ which belongs to the monoclinic prismatic type shows essentially the same structure but the oxygens are situated a little unsymmetrically round the chlorine atom. He further finds that in $KBrO_3$, Br—O is 1·68 A and in $NaIO_3$, I—O=2·87, 2·95 and 3·18A. Thus the distance of the halogen atom from the plane of the oxygens increases at first slowly, from Cl to Br and rapidly from Br to I. A similar remark has been made for the chlorides of P, As, Sb and Bi, where the Raman spectra have been interpreted as indicating that the distance of the central atom from the plane of the chlorine atoms increases with increase in atomic weight of the central atom.[3]

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[2] Zachariasen, Z. Krist., 71, 501, 517(1929).
Skr. Norske Videnskaps-Akad., I, 7-165(1928).

Comparison of ClO_3 and NH_3 groups :—Before discussing the relation between Raman and infra-red data in the case of these substances it will be useful to consider the possible vibrations of such a system as described above. NH_3 could be pictured as a similar type and the possible frequencies have been worked out by Dennison.[4] The molecule could be considered as a symmetrical tetrahedron with the N atom at the apex. Four active frequencies could be expected, two with their moment parallel and two with their moment perpendicular to the symmetry axis. These frequencies agree very well with the infra-red absorption maxima of gaseous ammonia examined by Barker, and are $\nu_1 = 10{\cdot}7\mu$, $\nu_2 = 6{\cdot}14\ \mu$, $\nu_3 = 2{\cdot}97\mu$ and $\nu_4 = 2{\cdot}22\mu$. The data of Daure on liquid ammonia show ν_1, ν_2, and ν_3, the last which is the strongest showing two more components.

We can now compare the frequencies of the ClO_3 group with those of ammonia. The values for the former are those of the single crystal examined by Daure[6] and of Dickinson and Dillon[7] for the solution. The infra-red data are those of Schaefer and Schubert[8] and of Laski[9].

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[3] Bhagavantam, Ind. J. Phys., *4*, 86(1930).

[4] Dennison, Phil. Mag., *1*, 195(1926).

[5] Daure, Trans. Farad. Soc., *25*, 827(1929).

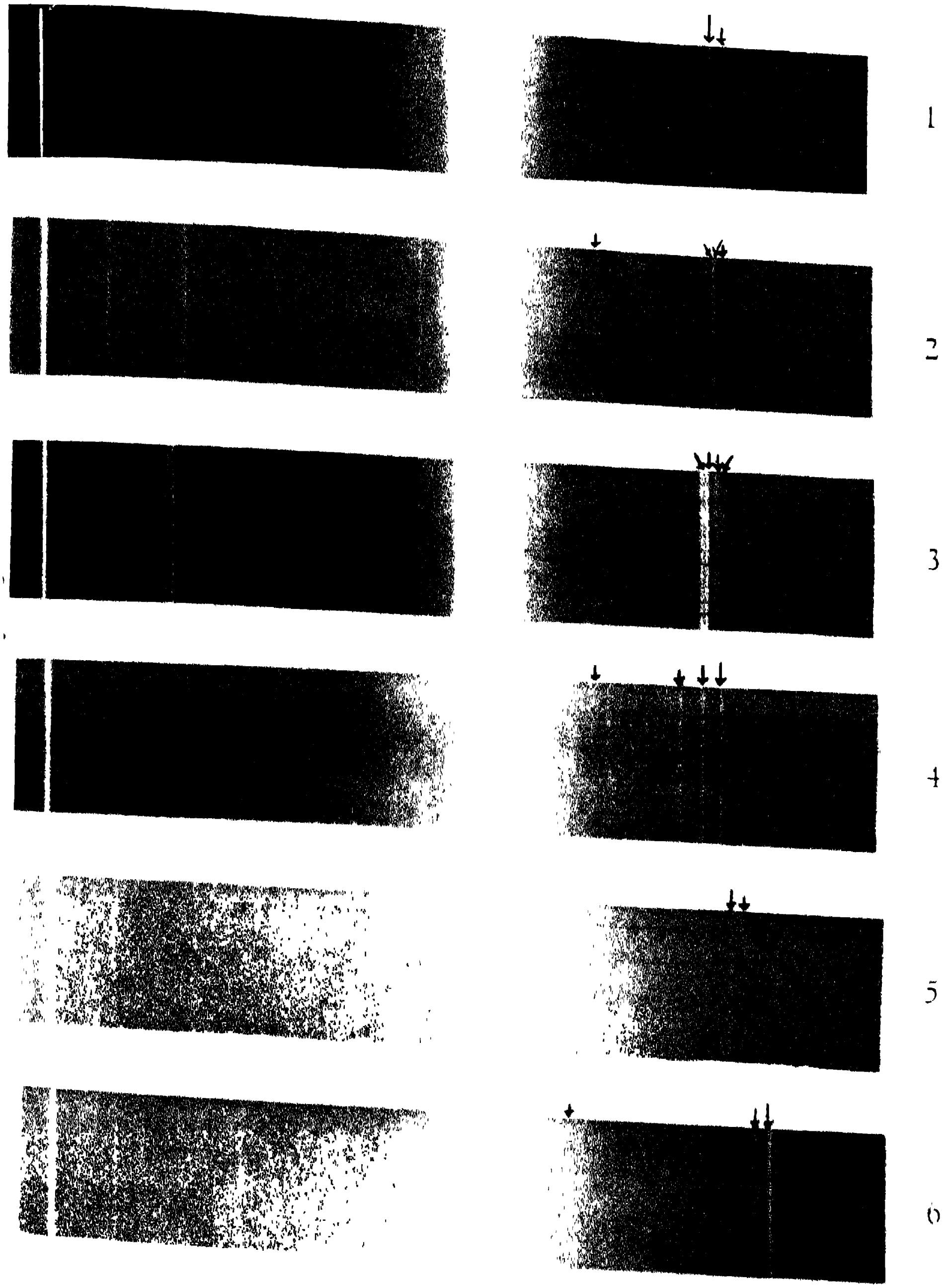
[6] Daure, Ann. de. Physique, *12*, 375(1929).

[7] Dickinson and Dillon, Proc. Nat. Acad. Sci., *15*, 334(1929).

[8] Schaefer and Schubert, Z. Phys. *7*, 309(1921)

[9] Laski, Z. Krist., *65*, 607(1927)

RAMAN Spectra of Crystals



1. Sodium Bromate. 2. Potassium Bromate.
3. Potassium Iodate. 4. Iodic Acid.
5. Potassium Periodate. 6. Ammonium Molybdate.

TABLE II

Frequency.	$\Delta\nu(\text{cm}^{-1})$ NH_3 liq.	$\Delta\nu(\text{cm}^{-1})$ ClO_3 cryst.	$\Delta\nu$ ClO_3, Soln.	Infra-red ClO_3 cryst.
ν_1	1070	484	479	400
ν_2	1680	625	611	625
ν_3	3210	936	932	996
	3300	970		
	3380	990		
ν_4	...	1025(?)	...	...

The analogy between these two cases is very striking. The intensity ratios between the components of the 10μ line in ClO_3 seem to depend on the environment of the ClO_3 group since they are comparatively stronger in the crystal than in the solution, analogous to the fact that ammonia at ordinary temperature shows one of the components of the $2{\cdot}97\mu$ triplet weaker and in the gaseous state only one frequency is observed.

Relation to Infra-red data :—The relationship between the the ClO_3, BrO_3 and IO_3 frequencies and the infra-red reflection data of Schaefer and Schubert could be next considered. The infra-red data show that while the 10μ frequencies in the cases of the chlorates are single, the bromates (some at least) and iodates show a splitting up into two components. The average infra-red wave-lengths increase when passing from Cl to Br to I. In a general way, the infra-red reflection data are in agreement with principal Raman frequency (ν_3) of the XO_3 ion. The Raman line shows a slightly higher infra-red wave-length which is probably due to the Forsterling-Havelock correction which has to be applied to the infra-red reflection maxima to convert them to absorption values. But when we come to the detailed structure of the lines, there are appreciable differences, especially with the bromates and iodates. This can be seen clearly from the values tabulated below. Only in the three substantes mentioned, comparative data are available. The infra-red data are those of Schaefer and Schubert.

TABLE III.

Substance.	ν_1	ν_2	ν_3
$NaClO_3$			
Raman.	484	625	936
Infra-red.	400	623	996
$NaBrO_3$			
Raman	371	...	797, 812
Infra-red.	...	435	817
KIO_3			
Raman	...	...	733, 751 784, 808
Infra-red.	...	...	801, 760

It could be seen in a general way that the infra-red data give the average of the group of Raman lines if they are close together. Further, the increase in infra-red wave-length when passing from ClO_3, BrO_3 to IO_3 is evident from both data. But what is very interesting is the strong frequency ν_3 and how the nature of that line changes remarkably with different central atoms. This fact seems to be intimately connected with the displacement of the central atom away from the plane of the oxygen with increase in the atomic number of the central atom. In ClO_3, ν_3 is quite sharp and its companions to the long wave-length side quite feeble. For BrO_3, one strong line and a weak but sharp companion on the long wave-length side is observed with $NaBrO_3$, while with $KBrO_3$ the strong line itself shows a companion to the short wave-length side in addition. In KIO_3, two pairs of lines one strong and one weak are observed, the mean separation between the groups being approximately the same as in $KBrO_3$. A unique explanation of all these various facts is not offered here, but this behaviour could be attributed to the unsymmetrical situation of the halogen atom with respect to the oxygens in the XO_3 group, as could be seen from the crystal structure data of Zachariasen (*loc. cit.*) and supported by comparison of Raman spectra data for crystals and solution. A similar doubling of ν_3 in Ba chlorate (monoclinic) is also observed in the present experiments.

It should be remarked in this connection that a comparative study of the compounds of the AX_3 type *e. g.* NH_3 the chlorides of P, As, Sb, Bi, SO_3 as well as the halogenates studied in this paper show that ν_3, the strong frequency is influenced both by the mass of the central atom as well as that of X. The present experiments indicate also that this frequency can show components which disappear in a dilute solution. The broadening and joining up of the close double lines in the halides of Sb and Bi noticed by Daure may not be due to dissociation (which can explain the faintness only), but due to the disappearance of the components, as found for example in the case of IO_3 group. Hence it seems likely that AX_3 group is distorted to a great extent in the crystal or liquid, this distortion becoming less when freed from the influence of its neighbours.

Comparison of data for crystals and solutions :—Next, the influence of dilution can be followed in some of these substances. The comparative data are given below.:—

TABLE IV.

Substance.	ν_1	ν_2	ν_3
$NaClO_3$			
Cryst.	484	625	936
Soln. (51%)	479	611	932
$NaBrO_3$			
Cryst.	371	...	797, 842
Soln. (26%)	367	...	810
HIO_3			
Cryst.	327		633, 713, 781
*Soln. (10%)	317	393	802 (broad)

* Nisi (*q. v.*)

There is very little change in the case of sodium chlorate on solution. In the solution of $NaBrO_3$, an average of the two lines is found in solution, while in HIO_3, the broad strong line at 800 wave numbers, represents an average of three strong lines with shorter shifts found in HIO_3 crystals. This value is also greater than the average of the four lines found in KIO_3 crystals. This shows clearly that the splitting up of ν_3 is essentially due to the distortion of the XO_3 group produced by the field of neighbouring cations.

Intensity of Raman scattering :—Finally the increase in intensities of the lines when passing from the chlorate to the iodate previously mentioned has to be explained. The present author has previously found that covalency is an essential condition for the emission of strong Raman lines. We know from the work of Fajans that covalency increases when passing from chlorine to iodine, *i.e.*, with increasing size of the atom. [10] This may be the explanation; or the more common one that with the increase in refractive index which accompanies substitution by heavier atoms, the classical and hence also Raman scattering should increase.

Till now, the inactive frequencies only were supposed to come out with great prominence in Raman spectra and *vice-versa*. While this is so in many cases, still, the present experiments show that the active frequencies can also come out with considerable intensities in the Raman spectra.

5. *Substances containing the XO_4 Group.*

A few perchlorates, potassium iodate, ammonium molybdate and sodium tungstate were examined. The results are set forth in the following table :—

Comparison with X-ray and infra-red data :—The sulphate ion could be regarded as typical of XO_4 group, and it has been shown to possess four fundamental frequencies. Sodium perchlorate is isomorphous with anhydrite or anhydrous calcium sulphate, and hence it shows corresponding Raman frequencies, except the one at about 9μ which is seen very feebly on the plate. X-ray measurements also indicate that the ClO_4 group is tetrahedral. Aqueous $HClO_4$ which has been examined by several investigators shows almost the same frequencies as those found in ammonium chlorate crystals. The slight decrease in frequency shift when passing from the sodium to the ammonium salt is also in harmony with previous observations on the sulphates and nitrates. As pointed out by Ramaswamy [11] in the case of sulphates, the ratios of the two inactive frequencies are very nearly 2 in accordance with the theoretical ratio of Dennison for methane.

[10] Sidgwick, " Electronic Theory of Valency ", p. 104.

[11] Ramaswamy, Ind. J. Phys., 5, 193 (1930).

TABLE V.

(*Exciting line*, 4358·34 I.A., ν=22938·1).

Substance.	Wavelength in I.A.	ν.	$\Delta\nu(cm^{-1})$.	λ in μ.	Intensity.	Remarks.
Sodium perchlorate $NaClO_4$, H_2O	4546·22	21990·1	948·0	10·55	Strong	Merck
Ammonium perchlorate NH_4ClO_4	4448	22476	462	21·6	Faint	Merck
	4482	22305	633	15·8	V. faint	
	4543·16	22005·0	933·1	10·72	Strong	
Potassium per-iodate KIO_4	4514·49	22144·6	793·5	12·60	Strong	Griffin
	4524·17	22097·3	840·8	11 89	Faint	Tetragonal
Ammonium*	4399·7	22722	216	46·4	Faint, br.	Merck. for analysis.
molybdate	4427	22582	356	28·1	V. faint. br.	$3(NH_4)_2O.7MoO_3.4H_2O$
	4532·17	22058·3	879·8	11·37	Med. str.	
	4543·00	22005·7	932·4	10·73	Strong	
Sodium tungstate $Na_2WO_4.2H_2O$	4542·10	22010·1	928·0	10·78	Strong	Merck.

* The formula is more complicated than $(NH_4)_2MoO_4$.

It will be useful to review the infra-red absorption data for some salts containing the AX_4 group given by Taylor.[12] K_2SO_4, K_2CrO_4, $KClO_4$ and $KMnO_4$ have been investigated by him and they all show very similar absorption curves. One notable feature in the curves is the presence of a very faint peak corresponding to the inactive frequency. This shows that we are not dealing with perfect tetrahedrons. The results are given below with slight changes in the assignments and omitting the combinational frequencies.

TABLE VI.

Frequency.	K_2SO_4	$KClO_4$.	$KMnO_4$.	K_2CrO_4.
ν_1	...	...	...	...
ν_2	625	720(?)	...	...
ν_3	980	930	833	787
ν_4	1092	1080	888	870

In addition, a peak at 788 wave numbers is found in the case of $KMnO_4$ which coincides with the frequency of vibration of the Mn atom within the tetrahedron (calculated from visible absorption bands). ν_1 is beyond the region of his measurement. ν_2 and ν_4 agree approximately with the infra-red reflection data of Schaefer and also with the lines in the Raman spectra.

When we come to consider the case of iodates, molybdates and tungstates, a complication ensues on account of the large size of the central atom; and we can no longer explain the frequencies on the same model as that for the sulphates and perchlorates. We have seen in the case of bromates and iodates that with the increasing atomic weight of the central atom it is more and more unsymmetrically removed from the plane of the oxygens. In the case of sodium tungstate, only one sharp line was obtained, the others probably being weak. Its frequency is the same as that for the chlorates in spite of the fact that the central atom is much heavier. Still, this may be an inactive frequency, since no infra-red maxima are found in that region.

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[12] Taylor, Trans. Farad. Soc., 25, 856 (1929).

TABLE VII

Substance	Infra-red max.	Strong Raman lines.	
K_2SO_4	1092	981	
$KClO_4$	1080	933	(amm. salt)
KIO_4	——	794	
$PbMoO_4$	851	932	(amm . salt
$CaWO_4$	800—860	928	(sod. salt)

Comparison of data for crystals and solutions :—The values for the Raman frequencies in the solids could be compared with their values in solution (the latter have been taken from Nisi).[13]

TABLE VIII

Substance	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	ν_4
NH_4ClO_4 cryst.	162	633	933	...
$HClO_4$ (30%) Soln.	164	628	934	1121
Na_2WO_4 cryst.	...	...	928	...
,, Soln. (20%)	...	...	931	...
KIO_4 cryst.	371	...	797, 842	...
,, Soln.	..	..	702, 806(?)	...
Amm. molybdate cryst.	216	356	880, 932	...
,, Solution (10%)	...	...	890, 944	...

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[13] Nisi, Jap. J. Phys., 5, 119 (1929).

The strong lines given by crystalline ammonium molybdate and sodium tungstate are approximately in the same position. The values for solutions agree fairly well except in the case of KIO_4 where Nisi expresses some doubt as to the origin of the lines in the dilute solution that he examined. It is very likely that the XO_4 group is much more distorted in these cases than if the central atom were Cl or S. In the case of KIO_4, the strong frequency has a faint component on the long wave-length side. Otherwise, its position agrees qualitatively when compared to those of SO_4 and ClO_4 groups. An accurate study of the nature of the groups in these crystals by means of X-rays would give us more insight into the nature of these oscillations.

Comparison of XO_3 and XO_4 groups. Dickinson and Dillon have remarked that the Raman lines given by these two types occur in almost identical positions except for differences in relative intensities of the less intense lines. This could be seen from their data for $HClO_4$ and $NaClO_3$ solutions. found a slight difference (about 10 wave numbers less) in the principal frequency when passing from SO_3 to SO_4. In the present experiments, a similar agreement is seen between the data for the chlorates and perchlorates. But the spectra of the iodates and periodates are entirely different, the prominent lines in the latter appearing at larger wave-length shifts. The agreement in the case of the chlorates and perchlorates is remarkable when we consider that the strong line in one case is an active vibration while in the other it is very nearly an inactive one. This agreement in the position of the lines is to be expected since the ClO_4 could be derived from ClO_3 simply by the addition of an oxygen atom without any change in the character of the ClO_3 group itself.

Other substances which belong to these groups *viz.* metaphosphates, orthophosphates, silicates and other oxides of the type X_2O_5 which are closely related to the XO_3 type are being investigated.

The author takes this opportunity of thanking Sir C. V. Raman, Kt., F.R.S., for inspiration and guidance during the course of this work.

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Raman Spectra of Inorganic Crystals : Part II.

Some Hydroxides, Cyanides and Sulpho-cyanides.

By

P. KRISHNAMURTI

(PLATE XXV)

(*Received for publication, 22nd September, 1930.*)

ABSTRACT.

Raman spectra of a few typical hydroxides, cyanides and sulphocyanides in the solid state have been studied by the crystal powder method. *Sodium hydroxide* gave a very strong and sharp line (3630 cm.$^{-1}$) attributable to the OH ion. In strontium and barium hydroxides examined as octohydrates, the faint lines (3484 and 3417 cm.$^{-1}$ respectively) could be attributed either to the water of crystallisation or to the OH ions.

Among the simple cyanides, *mercuric cyanide* gave a strong line due to the CN group (2192 cm^{-1}) and a weaker one (276 cm.$^{-1}$) attributable to the Hg-CN oscillation similar to the Hg-Cl oscillation previously observed by the author in $HgCl_2$ crystals (312 cm.$^{-1}$). A comparison of the existing data for the cyanides clearly show that the CN frequency is raised by *covalent bonds* between the CN group and other atoms or groups. $Hg(CN)_2$ which is shown by Raman spectra and its low conductivity to be covalent shows a high value nearer that of methyl cyanide.

The influence of *solution* on the highly ionised alkali cyanides or of the feebly ionised mercuric cyanide is very small. An intermediate case may be that of $KAg(CN)_2$ studied only in solution.

Among sulpho-cyanides, the potassium salt gave a strong line (2050 cm.$^{-1}$) and a weak one (747 cm.$^{-1}$) approximately in the same position as in a conc. solution. It is shown that the thio-cyanate ion could be pictured as $S=C=N$, the double bond between C and N explaining the lower frequency as compared to $C\equiv N$ ion. The weaker line is attributed to the S atom vibrating against the CN group as a whole. The same dependence of the frequency on the covalent nature of the atoms or groups joined to CNS group, by comparison of the values of K, NH_4 and Ba thiocyanates in the crystalline state is pointed out.

1. *Introduction.*

In a series of papers contributed to this journal, the present author has examined numerous inorganic salts of a simple type which contain particular groups like the nitrates,[1] sulphates, chlorates, bromates, iodates and perchlorates in the solid state, and attempted to correlate the Raman frequencies with the infra-red absorption bands. The influence of the cation on the characteristic frequencies of the anion, in the various crystals as well as the influence of solution on the Raman lines has been followed. In addition to these substances, the simpler cases of the inorganic halides as well as the element sulphur[2] (which however contains complex groups like S_{16} in the crystal), have been examined previously. The present investigation has been directed to the other simple types of compounds like the inorganic hydroxides and thiocyanates in the crystalline state.

2. *Previous Investigations.*

Hydroxides :—A diatomic group like the OH ion can have only one frequency, and it will be in the region of 3μ since it represents more or less the oscillation of the light hydrogen atom. For determining this frequency, the alcohols or phenols are unsuitable since several other hydrogen frequencies come in. Water is a more favourable case since the two hydrogens are joined to the oxygen atom. Concentrated aqueous solutions of sodium or potassium hydroxides may be interesting from this point of view, but they do not seem to have been studied.*

[1] Krishnamurti, Ind. J. Phys., 5, 1, 183 (1930).

[2] ,, ,, 5, 105, 113 (1930).

* Grantham, Phys. Rev., *18*, 339 (1921) gives infra-red absorption data.

Several investigations have been carried out on the structure of the water bands at about 3 μ. While Gerlach[3] and Meyer[4] find only two bands, Ganesan and Venkateswaran[5] find three bands, the last one being faint, the frequency shifts being 3199, 3453 and 3602 cm^{-1} respectively. The presence of the last band has of course to be confirmed by using monochromatic excitation *e.g.* Wood's helium line, since there is doubt in the above case whether it could not have arisen from the 4077 mercury line. For the water of crystallisation in gypsum, Dickinson and Dillon[6] find 3403 cm^{-1} medium, and 3491 strong. Krishnan[7] finds 3240 weak, 3397 strong diffuse; 3493 weak. Schaefer, Matossi and Aderhold[8] find only two bands of about equal intensity (3397 and 3510 cm^{-1}). There is wide divergence between all these three results.

The infra-red data of substances containing the OH group could also be considered here since that frequency should be active and hence should appear as an infra-red absorption band. Here also it is difficult to distinguish between the maxima due to the free and chemically combined water. We can confine our attention to the absorption of water vapour. Hettner explains the observed maxima in terms of two fundamentals $\nu_1 = 6.26\mu$ and $\nu_2 = 2.66\mu$. The 2.66μ absorption is the strongest one observed.[9] These results will be discussed in connection with the data obtained by the author with Na, Sr and Ba hydroxides in the solid state.

Cyanides and Sulphocyanides :—Like the OH ion, the CN ion could be expected to have a single frequency, being a diatomic group, and we can expect the frequency to be an active one. Extensive data on the frequencies of the CN group as found in liquid organic cyanides and of solutions of simple and complex cyanides are available [10, 11]. The existence of one frequency at about 4.3—4.8μ depending on the nature of the other atoms linked to the cyanogen group is found in all of them. The infrared absorption of HCN and of cyanogen also show maxima at about 4.8μ and 4.65μ respectively.

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[3] Gerlach, Phys. Z., *31*, 695 (1930).

[4] Meyer, Phys. Z., *31*, 699 (1930).

[5] Ganesan and Venkateswaran, Ind. J. Phys., *4*, 195 (1929).

[6] Dickinson and Dillon, Proc. Nat. Acad. Sci., 15, 695 (1929).

[7] Krishnan, Ind. J. Phys., *4*, 131 (1929).

[8] Schaefer, Matossi and Aderhold, Phys. Z., *30*, 581 (1929).

[9] Schaefer and Matossi, ' Ultrarote Spektrum, ' p. 287 (Springer, 1930).

The sulphocyanides in aqueous solution show the cyanogen frequency, and another fainter one at about 740 cm^{-1} attributable to the S—CN oscillation. Phenyl isothiocyanate shows also these frequencies in addition to numerous other ones.

In the present investigation, many of the substances examined in solution as well as some new ones have been studied in the solid state in the form of coarse crystals or crystalline aggregates. The data of the previous investigators on the solutions are given in the discussion wherever necessary.

3. *Experimental Technique.*

The arrangements were essentially the same as described in the previous investigation.[12] Two pyrex glass lamps were used to give intense illumination. The incident mercury lines in the region of 4916 had to be removed with a filter since the the OH and CN lines happened to fall in that region. For this purpose the following filters were used :—

(a) A very dilute solution of uranin (sodium salt of fluorescein) followed by an ordinary blue glass to cut off the green fluorescence. This cleared the whole region round about 4916 without weakening the 4096 or the 4358 lines appreciably.

(b) A dilute solution of o-cresolphthalein (sodium salt). The 4046 line was weakened considerably, the 4358 line being very little weakened. The whole region after 4700—4800A was also completely cleared .up. It is an efficient monochromatic filter and its use has now been suggested for the first time.

In order that the lamps could be brought as near as possible to the substance, the solution was placed between two

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[10] Petrikaln and Hochberg, Z. Phys. Chem., 8 (B), 440 (1930)

[11]. Pal and Sengupta, Ind, J. Phys., 5, 13 (1930).

[12]. Krishnamurti, Ind. J. Phys., 5, (1930).

glass plates about 2 mm. apart separated by a washer of non-vulcanised India-rubber. The sides were then sealed up with sealing wax. Since the fan was cooling the arc lamps when working, the filters remained intact. In the case of sodium hydroxide and other hydroxides, a triangular glass cell cemented together on all sides except one was used. After the substance was introduced, the side was closed with a metal cap and made air tight by applying a layer of paraffin. An average exposure of 1½ to 2 hours was given in each case.

4. *Resutts.*

The following substances were examined. All of them are Merck's specimens except Hg $(CN)_2$ which was of Kahlbaum's origin. Sodium hydroxide, barium and strontium hydroxides (hydrates), sodium and mercuric cyanides; potassium ferrocyanide (the Hg 5461 line was used in this case); a concentrated aqueous solution of KAg $(CN)_2$; potassium, ammonium and barium thiocyanates. An iron arc comparison spectrum was taken on each plate and the lines measured by linear interpolation between the two nearest known iron lines.

TABLE I.

Hydroxides, Cyanides and Sulphocyanides.

Substance.	Exciting line in I.A.	Raman line in I.A.	ν	$\Delta\nu$ (cm^{-1})	λ Infra-red in μ.	Intensity.
NaOH Sodium hydroxide	3650·15	4207·7	23759	3630		Med. str.
	3654·83	4213·7	23725	3629		,,
	4046·56	4743·59	21075·1	3630·3	2·755	Strong.
Sr (OH)$_2$, 8H$_2$O Strontium hydroxide	4046·56	4711	21221	3484	2·870	Faint.
Ba(OH)$_2$, 8H$_2$O Barium hydroxide	4046·56	4696	21289	3417	2·927	V. faint.
NaCN Sodium cyanide	4358·34	4794·02	20853·5	2084·6	4·807	Med. str.
KAg(CN)$_2$ Aqueous solution	4358·34	4806·5	20799	2139	4·686	Faint, broad.

$Hg(CN)_2$ Mercuric cyanide	4046·56	4440·53	22513·5	2191·9	4·562	Med. str.
	4358·34	4818·7	20746·6	2191·5		,,
	,,	4411·37	22662·3	275·8	36·3	Faint.
$K_4Fe(CN)_6$, $3H_2O$ Pot. ferrocyanide	5460·74	6191·6	16146·5	2161	4·627	Faint.
KCNS Potassium thiocyanate	4046·56	4412·78	22655·4	2050·0	4·678	Strong.
	4358·34	4786·08	20858·1	2050·0	,,	Strong.
	,,	4505	22191	747	13·39	Faint.
NH_4CNS Ammonium thiocyanate	4046·56	4416	22639	2067		
	4358·34	4790	20871	2067	4·838	Faint, br.
$Ba(CNS)_2$ Barium thiocyanate	4358·34	4511	22162	776	12·88	V. faint.
	,,	4786·8	20885	2053	4·871	Med. str. broad.

5. *Discussion of Results.*

Hydroxides :—The most striking result was the appearance of a strong sharp line (excited by the 4046A) with NaOH. Merck's pure specimen in the form of small translucent tablets was used in the air tight container mentioned above and using filter (*a*). The two lines excited by 3650 and 3655 lines were also visible on the plate and confirmed the assignment. This frequency (3630 cm^{-1}) should hence be attributed to the OH ion. This corresponds roughly to 2·66μ infra-red absorption of water vapour found by Hettner, though the two types of oscillations are quite different. It will be interesting to study the changes in position and intensity of this line with various other cations like Li or K. The other two hydroxides studied consisted of the octohydrates. They showed each a faint broad line at a smaller wavelength (Sr, 3484 cm^{-1} ; Ba, 3417). It is difficult to say whether this represents the frequency of the OH ion or of the water of crystallisation, especially as we see that in gypsum the strong broad line due to water of crystallisation may be between 3400-3500 cm^{-1}. But it is seen that with increasing mass of the cation, the frequency shift becomes smaller.

Cyanides and sulphocyanides :—The previous investigators have found one principal frequency for the CN group, though a feebler one (837 cm^{-1}) has been recorded for KCN.[13] But this line occurs in exactly the same position as a strong frequency in KCNO (838), and commercial samples of KCN are likely to contain the cyanate.[14] Still, it may be a genuine frequency, connected with the oscillation of $(CN)_2$, as we find a similar line for liquid cyanogen. We can confine our attention for the present to the principal frequency of the CN group and follow its changes through a series of compounds. The following tables summarise the results of the author on crystals as well as those of others on the solutions or pure liquids containing CN and CNS groups.

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[13] Pal and Sen Gupta, *loc. cit.*

[14] Mellor, Modern Inorganic Chemistry ; p 764 (Longmans, 1919)

TABLE II.

Cyanides.

Substance.	P. and H.	P. and S.	Author.
Dicyanogen	2334	......	.. ..
CH_3. CN	2250	2256	......
C_6H_5.CN	2234	......	. . ..
$Hg(CN)_2$	2204	..... .	2192*
$K_4Fe(CN)_6$	......	......	2161
$KAg(CN)_2$	2124	2109	2139
NaCN	......	......	2085
KCN	2082	2080	... ..

P. and H.—Petrikalu and Hochberg.
P. and S.—Pal and Sengupta

* Woodward, Phys. Z., 31, 792 (1930) gives 2195 cm^{-1} for an aq. soln. of $Hg(CN)_2$.

TABLE III.

Sulphocyanides.

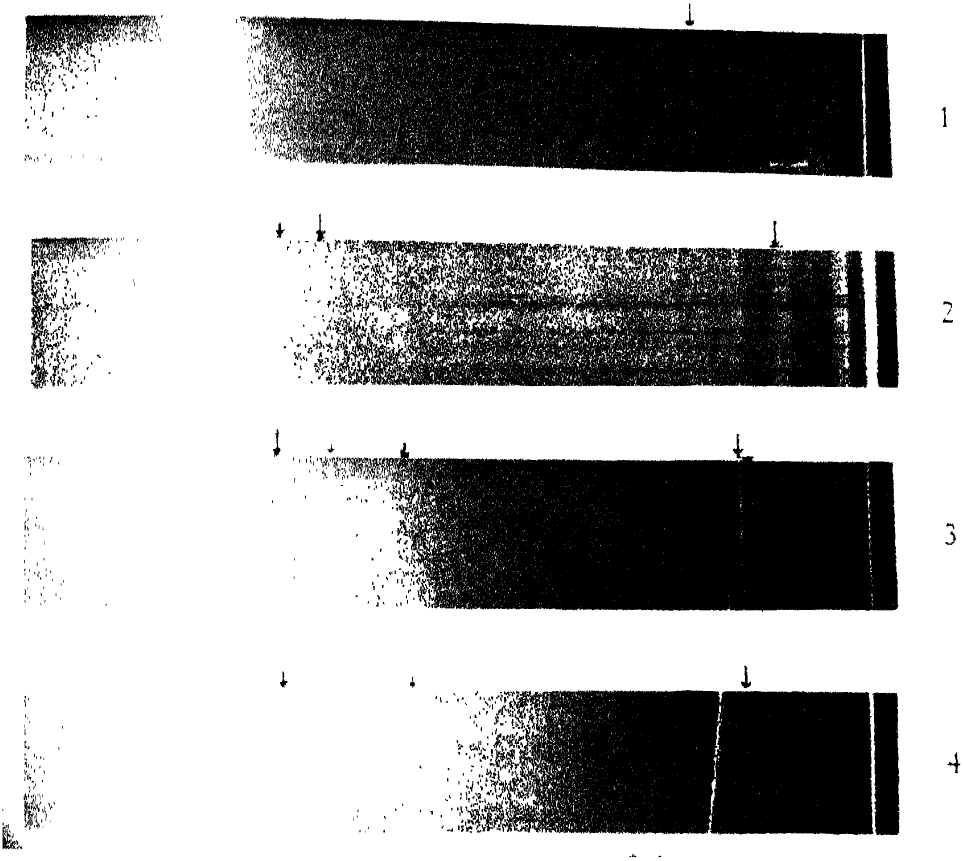
Substance.	P. and H.	P. and S.	Author.
CH_3.SCN	2155	......	......
C_6H_5.NCS	2092 (broad)	2067 (broad)	.. ..
NH_4CNS	......	2066 str 743 w.	2067
KCNS	2057	..	2059 str 747 w.
$Ba(CNS)_2$	......	......	2053 br. 776 w.

Of the cyanides examined by the author $Hg(CN)_2$ crystals gave the intense CN frequency (2192 cm^{-1}) excited by the 4046 and 4358 lines. In addition it showed another fainter line (276 cm^{-1}) which could be attributed to the Hg-CN oscillation, by analogy with case of $HgCl_2$ studied by the author which showed a similar oscillation (312 cm^{-1}). It is difficult to say just now whether it is an active or inactive frequency, *i.e.*, whether the model is a linear or bent one, but its analogy with $HgCl_2$ in several properties, especially its poor conductivity, shows that the molecule may have the same linear type.

Covalency and the Raman effect :—A glance at Table 1 will show many interesting relationships. One is that the frequency shift is highest with those substances where the CN group is combined covalently with the remaining groups. These substances possess the typical properties of covalent compounds, *i.e.*, are easily volatile and are non-conductors. $Hg(CN)_2$ belongs to this group, being very little ionised, its covalent nature being clearly seen by the presence of a frequency at 276 cm^{-1}due to the Hg-CN oscillation. Hence the large frequency shift observed ($\Delta\nu = 2161$) when compared to the normal value, *i.e.*, of CN ion in a solution of KCN (2080). The values obtained for $KAg(CN)_2$ solution vary within rather wide limits showing that it may depend on the concentration of the solution or the relative quantities of KCN and Ag CN present. The value is intermediate between that of mercury and potassium cyanides. The value for $Fe(CN)_6$ is near that for $Hg(CN)_2$ as is to be expected since both groups are very little ionised in solution.

The influence of solution seems to be very small for either the highly ionised alkali cyanides or for the poorly ionisable $Hg(CN)_2$. The latter does not show much change either in methyl alcohol solution or aqueous solution. The cases of partially ionised cyanides will be interesting since intermediate values could be expected depending upon the degree of ionisation in the crystal.

RAMAN Spectra of Crystals



1. Sodium Hydroxide. 2 Mercuric Cyanide.
3. Potassium Thiocyanate. 4. Barium Thiocyanate.

Coming to the thiocyanates, we find that KCNS crystals give an intense sharp line (2050 cm^{-1}) and a faint one (747 cm^{-1}). The former has a slightly smaller value than the value for CN group (2080 cm^{-1}). We see however that in methyl cyanide CH_3-CN, the CN frequency is more than in CH_3-SCN by about 100 wave numbers. Still the value for the latter is higher than for CN ion as is to be expected if CH_3S is taken as one group united covalently to CN. But it will be seen that when this covalent binding becomes weaker or becomes electro-valent, the value falls below that for the free CN ion (less than 2080). This is because even though there is covalent binding between CN and S it is now joined to a divalent atom, and hence in S=C=N, since there is only a double bond between C and N, its frequency is naturally lowered. The smaller frequency (747 cm^{-1}) observed in the thiocyanates could be attributed to the S=CN oscillation.

Just as with cyanides we find in this case also a rising up of the frequency in covalent compounds and an approach to normal value in electro-valent or fully ionised ones. Ammonium thiocyanate (salt composed of a weak acid and weak base) gives a distinctly higher value in the solid state than KCNS. If the crystals had been fully ionised, then the influence of the cation will be in the opposite way as we see in the inorganic sulphates and nitrates.[15]

Usually, the increasing charge on the cation is to increase the frequency, but with increasing size it is reduced. Taken together with the degree of ionisation in the crystal, the frequency observed in Ba $(CNS)_2$ is due to the combined influence of all the three factors. The line is much broader than in the uni-valent compounds though it is in approximately the same position. The fainter line due to S=CN oscillation shows a distinctly higher frequency and the influence of the ion is felt more by this oscillation than by that of the cyanogen group.

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[15] Krishnamurti, *loc. cit.*

In this connection, it will be interesting to study the Raman spectra of Li cyanide and sulphocyanide in the solid state, since we know from the work of Fajans [16] that the smaller the cation the greater will be the tendency to covalent formation. HCN liquid like the case of HNO_3 could be expected to show a strong line near the frequency observed for CN ion, and this seems to be actually the case.[17] The present investigation has been limited by the number of substances readily available, and it is hoped at a later date to prepare a complete series of compounds containing the CN and CNS groups, and trace the influence of the cation and the extent of the covalent linking between the metal atom and these groups as shown by the displacement or broadening of the Raman lines.

The author's warmest thanks are due to Sir C. V. Raman, F.R.S., for his keen interest and guidance in this investigation,

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[16] Fajans, Z. Phys., 23, 1 (1924)

[17] Recently studied by Dadieu and Kohlrausch.

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On the Relative Intensities of Different Raman Lines due to Different Exciting Frequencies.

By

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(*Received for publication, 24th September, 1930.*)

Abstract.

The ratios of the absolute intensities of the two Raman lines due to nitrobenzene shifted by 1342 and 1582 wave numbers have been measured in the case of the exciting Hg lines 5461 A.U. and 4358·6 A.U. and have been found to be 6·5 : 2·74 and 15·9 : 3·1 respectively. The probability of the intensity of the Raman line shifted by 1342 wave numbers being abnormally great in the case of the exciting line 4358·6 A.U. is discussed.

1. *Introduction.*

It has been pointed out in previous communications[1] that in the case of certain liquids, the Raman lines excited by the Hg line 3132 A. U. are much more intense than is indicated by the Rayleigh fourth power law relative to those excited by the Hg line 4358·6 A.U. and that the extent of deviation is different for different Raman lines. It has also been suggested that the presence of absorption in the ultra-violet region of the spectrum may be responsible for this peculiar behaviour of the Raman lines in that region. From this point of view it is expected that in the case of liquids having absorption in the visible region of the spectrum, the Raman lines excited by Hg lines in the visible region will exhibit this peculiar behaviour.

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[1] S. C. Sirkar, Ind. J. Phys. 5, 159, 1930; 5, 593, 1930.

It is, however, difficult to determine accurately to what extent the Rayleigh fourth power law is violated in the case of liquids having large absorption co-efficient for the visible rays, because the incident beam, while penetrating the liquid, is absorbed appreciably and the effective intensity of the incident beam is not accurately known. But inspite of this difficulty, it is quite easy to demonstrate that different Raman lines are not scattered according to the same law. If we choose a suitable liquid so that in the scattered spectrum there are two intense Raman lines very close to each other and if these are not scattered according to the same law, the ratio of the intensities of these two lines will be different in the case of different exciting lines. Such a suitable liquid has been chosen in the present investigation and the relative intensities of two Raman lines, very close to each other, have been measured in the case of two exciting lines in the visible region of the spectrum.

2. *Choice of the Liquid and Experimental Results.*

Liquids absorbing the violet and blue rays are generally coloured yellow or greenish yellow. On examining a few spectrograms[2] of light scattered by a few such liquids it was found that in the scattered spectrum of nitrobenzene, there are two Raman lines very close to each other, and these lines are so intense that they are excited strongly by both the Hg lines 4358·6 A.U. and 5461 A.U. This liquid was therefore selected as a suitable liquid for the present investigation. Nitrobenzene obtained from a fresh bottle was distilled in vacuum and the photograph of the scattered spectrum was obtained on a plate taken from a calibrated packet of Ilford panchromatic H and D 2,000 plates, the arrangements being exactly the same as those in the previous experiments.[3] The quartz wedge was placed in its usual position in contact with the slit and a clean glass plate was placed between a Heraus mercury lamp and the quartz tube containing the liquid in order to cut off the ultra-violet rays which might effect some photochemical change in the liquid. In the previous experiments,[3] as well as in the present investigation, a Fuess quartz spectrograph was used. The undisplaced scattered lines were also photographed on the same plate in order to compare their relative intensities. It was found that the Raman line shifted by 1342 wave numbers excited by the Hg line 4358·6 A.U. was stronger than that excited by the 5461 A.U. line though the undisplaced line 4358·6 A.U. was weaker than the undisplaced 5461 A.U. line. As in the incident spectrum the 4358·6 A.U. line was much stronger than the 5461 A.U. line, the effect of superposition of stray diffused light on the scattered beam would be to increase the relative intensity of the undisplaced 4358·6 A.U. line. It was actually not possible to avoid all the stray light and since inspite of the presence of stray diffused light, the 4358·6 A.U. line was weaker in the scattered spectrum, it was thought that the absorption co-efficient of the liquid for this wave length was fairly large. The absorption co-effieient of freshly distilled nitrobenzene was determined roughly with a Hilger Nutting photometer for the wave length 4358·6 A.U. using a Hg arc as source of light, and for the wave length of the Raman line in question, excited by 4358·6 A.U. line, using a pointolite lamp as source of light. The absorption co-efficient in the two cases were found to be 0·6 and 0·09 respectively. The increase of absorption co-efficient in the neighbourhood of the 4358·6 A.U. line is thus to some extent responsible for the comparatively small intensity of this undisplaced line in the scattered spectrum. As the absorption co-efficient for any wave length in the blue region was found to increase when the liquid was exposed to strong light for a long time, it was not possible to determine whether this Raman line excited by 4358·6 A.U. line was scattered according to the Rayleigh fourth power law relative to the same line excited by the 5461 A.U. line. On carefully examining the spectrogram, however, it was found that the ratios of the intensities of the two Raman lines shifted by 1342 and 1582 wave-numbers were quite different in the case of the two exciting lines 4358·6 A.U. and 5461 A.U. The photographic intensities of these two Raman lines were measured in the case of both the exciting lines in the same way as in previous experiments and the results given in Table 1 were obtained. I_1 and I_2 in Table 1 represent the photographic intensities of the Raman lines shifted by 1342 and 1582 wave numbers respectively.

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[2] The author's thanks are due to Dr. A. S. Ganesan and Mr. S. Venkateswaran for kindly allowing him to examine their original negatives.

[3] S. C. Sirkar, *loc. cit.*

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[3] S. C. Sirkar, *loc. cit.*

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TABLE 1

Exciting line in A.U.	I_1	I_2	I_1/I_2
4358·6	15·9	3·1	5·1
5461·0	6·5	2·74	2·37

The photographic sensitivities of the plate were determined for the wave lengths of the Raman lines in the case of both the exciting lines and it was found that the change in photographic sensitivity in passing from one of the Raman lines to the other was exactly the same in the case of both the exciting lines. The relative photographic intensities given in Table 1 thus give also the relative absolute intensities of the Raman lines.

Another source of error which might make the results given in Table 1 spurious, is the superposition of some incident Hg lines on one of the Raman lines. In order to eliminate this doubt, a photograph of the scattered spectrum was taken with a Fuess glass spectrograph having large dispersion, and on comparing with the incident spectrum, it was found that the incident Hg line 5889.1 A.U. almost coincides with the Raman line shifted by 1342 wave numbers and there is no Hg line in the region where the other Raman line lies. These faint incident Hg lines were not visible on the plate from which the results given in Table 1 were obtained and therefore these results are not affected at all by the presence of an incident line at 5889.1 A.U.

3. *Discussion.*

The Raman line shifted by 1342 wave numbers corresponds to the active frequency of the NO_2 group. The ratio of the intensities of this line for the two exciting lines 5461 A. U. and 4358·6 A.U. is about 6.5 :16, but that for the weaker Raman line is 2·74 : 3·1. Any one of the following two causes would make the ratio unequal in the case of the two exciting lines. Either the stronger Raman line is scattered with unusually great intensity in the case of the exciting line 4358.6 A. U., the other Raman line being scattered normally, or the latter Raman line is scattered with abnormal intensity in the case of the 5461 A.U. line, the stronger Raman line being scattered normally. As it has been observed in the case of some other liquids that some of the Raman lines are scattered with abnormally great intensity in the case of exciting wave lengths which are slightly absorbed by the liquids, it can be inferred that the Raman line corresponding to the active frequency of the NO_2 group is scattered with abnormally great intensity in the case of exciting line 4358.6 A·U. The NO_2 group is responsible for the colour of the liquid and absorption of the violet and blue rays. It is therefore quite natural that it is the Raman line corresponding to the active frequency of the NO_2 group which would behave abnormally in the neighbourhood of absorption.

It has been pointed out previously that in the case of benzene and cyclohexane, one of the Raman lines deviates more from the fourth power law relative to the 4358·6 A.U. line than others, in the case of exciting lines in the ultra-violet region of the spectrum. This is another way of saying that the ratio of the intensities of the different Raman lines does not remain constant for different exciting frequencies. The results of the present investigation thus lend support to the conclusions arrived at in previous communications.

The author is indebted to Prof. Sir C. V. Raman, F.R.S. for his kind suggestions and guidance.

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Pleochroic "Giant" Halos in Cordierite.*

BY

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AND

C. MAHADEVAN, M.A.

(Plate XXVI.)

ABSTRACT.

In the course of the examination of more than 200 halos contained in 20 thin sections of cordierite-gneiss from Madura District, South India, a few "giant" halos—those having dimensions larger than for normal ranges of α-particles in U and Th series—were observed, in addition to the normal halos. In view of the good agreement of the dimensions of these halos with the values theoretically calculated for the long range α-particles, it is conclusively shown that they correspond to the ranges of 9·3 cm. for RaC′ and 11·5 cm. for ThC′ in air. The richness of this cordierite in radioactive materials and the long period of activity of the latter (since Archaean times) have contributed to the full development and preservation of the structures in these halos. The relationship of the intensity of pleochroism of the halos to the directions of absorption in the crystalline medium in which they develop is incidentally referred to.

1. *Introduction.*

In a previous paper on pleochroic halos [1] occurring in the cordierite of a cordierite-gneiss from Madura District, South India, the presence of normal halos, similar to those described

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[*] Paper presented before the Geology Section, Indian Science Congress, Nagpur (1931).

[1] C. Mahadevan, Ind. Jour. Phys., I, pp. 445-456 (1927).

by Joly and others in biotite, etc., was recorded. It was shown there that, contrary to the observations of Joly and Fletcher,[2] the structures in cordierite were quite as well preserved as in biotite, and the peculiarities such as bleaching, emanation halos and dwarfs were clearly identified. The great sensitiveness of cordierite to α-rays and the absence of strong body-colour in the mineral in thin sections, have been favourable for observing and recording delicate structures such as the rings due to the extraordinarily long range α-particles of the U and Th series. In this paper, the results of a study of such long-range halos are discussed.

Joly[3] noted that outside the pupil, the ring due to Th C_2 appeared as a penumbra-like band, but the accentuation of the extreme margin was less definite than in the case of the U halo. Iimori and Yoshimura[4] obtained more definite evidence of rings with ranges longer than the ones attributable to the normal ranges of Th and U. In recent years the existence of such long range α-particles has been established by several workers, but the occurrence of halos corresponding to these ranges, in minerals, does not seem to have been so far definitely shown. During the course of the present work, we came across halos with well preserved structures where the outermost rings gave dimensions larger than those referable to the normal ranges of Th C′ and Ra C′. The inner rings correspond well with the known normal ranges of Th and U series respectively, while the outermost rings show a striking agreement with the long ranges for the same series.

2. *Results.*

Over 200 halos in various stages of development, contained in 20 thin sections of cordierite-gneiss from the above-mentioned locality, were carefully studied. The radial measurements were made with a Leitz petrographic microscope with No. 2 eyepiece and No. 5 objective, using an eyepiece-micrometer which was calibrated by means of a stage micrometer with 200 divisions to 2 mm. The above combination of eyepiece and objective was found to give satisfactory magnification and definition, and readings correct to 0·002 mm. could be obtained. Some measurements were also carried out by means of a Zeiss screw-micrometer ocular, and on comparison it was found that the combination first used was equally accurate. The measurements of the halo rings were made independently by each of us, showing close agreement.

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[2] Phil. Mag., 19, p. 635 (1910).

[3] Phil. Trans. Roy. Soc., A. 217, p. 70,(1918).

[4] Sci. Pap. Inst. Phys. Chem. Res., Vol. 5, No. 66, p. 17, (1926).

The cordierite under discussion is itself distinctly, though faintly, pleochroic in thin sections, the colours being a delicate pale lavendar-blue and a pale creamy yellow, the latter almost unnoticeable, except when contrasted by an adjoining colourless mineral like quartz or felspar. The pleochroic halos are brought out prominently when the direction of vibration of the polarised light is parallel to the direction of maximum refractive index in the mineral section. Dana and Ford[5] note that the halos are best seen in sections of cordierite parallel to the *c* axis, that is to say in sections where the birefringence approaches the maximum of the mineral. Rosenbusch and Mügge[6] observe that the halos are strongest in sections parallel to (100) in which the birefringence is ·0080—·0090, whereas they are scarcely noticeable in sections parallel to (001) where the birefringence is very weak (·0011—·0035). The depth of colour exhibited by the halo is therefore closely connected with the absorption and birefringence of the particular section of cordierite crystal in which it occurs.

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[5] "Textbook of Mineralogy," p. 497, New York (1922).

[6] "Mikroskopische Physiographie der petrographisch wichtigen Mineralien," Bd. I. Spez. Teil, p. 377, Stuttgart (1927).

In the course of the work it was also noted that, in some cases, the structures in halos which were made out with difficulty in ordinary polarised light, became accentuated when the nicols were crossed. The measurements of the radii of the different rings were always carried out with the polariser on, the aid of the analyser being sought occasionally for bringing out any additional structures.

In several of the halos measured, the nuclei are of large dimensions. The measurements were all made from the nuclear edge to the several rings, having the micrometer scale divisions tangential to the edge. It was found that these readings show a fair agreement with the theoretical values. No nuclear corrections were carried out but the errors due to this, if any, can only have the effect of increasing the readings given here.

To calculate the theoretical values of the halos in the mineral due to the α-ranges of the members of the two series, the following method was used: the square root of the weight of the constituent atoms of the mineral was determined from the chemical analysis of this cordierite by one of us.[7] Its density was found to be 2·6. Bragg and Kleeman's value for the square root of atomic weight of air (3·79)[8] was assumed. From the above data, the range in cordierite corresponding to a range of one cm. in air at 15°C. was obtained from the formula :—

$$L=\frac{D}{d}\times\sqrt{\frac{M}{m}}$$

where L = the range in cordierite corresponding to a range of 1 cm. in air at 15°C.

D = density of air at 15°C.

d = density of cordierite.

M = atomic weight of cordierite.

m = atomic weight of air.

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[7] M. S. Krishnan, Mineral. Mag. XX, No. 107, p. 249 (1924).

[8] W. H. Bragg and R. Kleeman, Phil. Mag. 10, p. 336 (1905).

The value of L in the present case is found to be 0·005594 mm. This result, multiplied by the ranges of α-rays for the various members of the U and Th series, gave the theoretical values in cordierite.

3. *Uranium Halos.*

A large number of normal halos have been measured, many of these giving the ring due to RaC in addition to the inner rings. Bleached halos are also met with fairly frequently. In addition, there were some typical "Emanation" halos showing the inner ring due to RaEm, usually of a bluish grey tint, and the outer intense yellow ring due to RaC and RaC′. A large number of "dwarf" halos were also met with, a description of which is reserved for a future communication.

The most noteworthy result of this study is the identification of several well preserved "giant" halos. In these, the outermost ring is generally of an intense yellow colour grading off imperceptibly towards the outer margin. The readings have in all cases been taken to the limit of distinct visibility, and it is possible that the actual extent of the halos is slightly larger than the measurements given here. Within some of these "giants," three or four inner rings can be made out, the innermost being greyish, the next often bleached, and the third light yellow.

The readings for the outermost halo in the case of the U "giants" range from 0·050 to 0·055 mm., the inner rings, where present, showing good agreement with the different members of the U series.

4. *Thorium Halos.*

Quite a large number of Th normal halos have been measured, but only a few cases of "giants" came under observation. In a typical case (fig. 6) three very distinct rings were observed with radial measurements of ·013 mm. (grey), ·025 mm. (faint yellow) and ·067 mm. (intense yellow). The very small proportion of Th "giants" to normal halos is in marked contrast with a much higher proportion of U "giants" to U normal halos.

5. *Discussion.*

The identification of long range α-particles was first due to Rutherford and Wood [9] who obtained, from Th active deposits, ranges of 10·2 cm. and 11·3 cm. in air at 15°C and 760 mm. pressure. In 1919 Rutherford [10] isolated the long range particles from Radium active deposits. Later, Rutherford by himself,[11] and in collaboration with Wood,[12] and with Chadwick,[13] carried out further studies on the long ranges. Bates and Rogers [14] recognised the existence of several groups of long range α-particles, the 9·3 cm. range for RaC and the 11·5 cm. range for ThC being the most common amongst the long ranges of these two series. Yamada,[15] from more critical work, established with certainty ranges of 9·3 cm. in RaC and of 11·5 cm. in ThC, and mentioned that groups with longer ranges could not be definitely established. All these observations were by the scintillation method.

Later investigators, notably Meitner and Freitag,[16] using the expansion chamber method, detected two groups of particles with ranges of 11·5 and 9·5 cm. respectively for ThC. Philipp [17] confirmed their observations using the scintillation method. He also identified ranges between 9·5 and 12 cm. for

[9] Phil. Mag., 31, p. 385 (1916).

[10] Phil. Mag., 37, p. 571 (1919).

[11] Phil. Mag., 41, p. 570 (1921).

[12] Phil. Mag., 41, p. 575 (1921).

[13] Phil. Mag., 48, p. 509 (1924).

[14] Proc. Roy. Soc., A. 105, pp. 97-116, 360-369 (1924).

[15] Jour. de Phys., 6, p. 380 (1925).

[16] Zeit. f. Phys., 37, p. 481 (1926).

[17] Zeit. f. Phys., 37, p. 518 (1926).

RaC. Recently, Philipp and Donat[18] have confirmed the greater frequency in RaC of the 9·3 cm. range than the 11 cm. range. Finally, we may refer to the work of Nimmo and Feather[19] who have established ranges for ThC of 11·70 and 9·90 cm. with a few rays of greater than 12·5 cm. For RaC they obtained with certainty a range of 1·96 cm. and also strong indications of groups of α-rays with ranges up to 12·5 cm. The results of all these observers are given in Table I.

From the above resumé of the work on long range α-particles it is seen that the 9·2 cm. range in RaC and the 11·5 cm. range in ThC are the more frequent.

The calculated radii of the halo rings in cordierite corresponding to the above long ranges are given in Table IV. A comparison of these with the measurements for the "giant" halos shows a very satisfactory agreement. Thus, while the observed values for U "giants" range from 0·050 mm. to 0·055 mm., the calculated values lie between 0·051 and 0·053 mm. (see Table II). For ThC, the observed values are 0·061 and 0·067 mm., the corresponding calculated values being 0·063 and 0·065 mm.

The occurrence of uranium halos of larger dimensions than those corresponding to the normal ranges of α-particles of U was noted by Joly as early as 1910 (Phil. Mag., XIX, p. 328) but he suggested the possibility of Th being responsible for these outermost rings. Iimori and Yoshimura[20] who obtained more definite evidence of such halos explained away their presence by assuming that "the principal radioactive constituents in the nucleus accidentally happened to diffuse into the surrounding micaceous matter." They have also actually contested the view that they may be due to the long range α-rays. If their assumption has any basis, we should expect to find either the halos distorted in one direction towards which the radioactive matter diffused, or a corresponding increase in all the rings if the diffusion had taken place in all directions. Such a reasoning for explaining apparent discrepancies seems to us artificial and unsound. The real explanation seems to be on the lines indicated by Joly.

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[18] Zeit. f. Phys., 52, pp. 759-766 (1929).

[19] Proc. Roy. Soc., A. 122, pp. 668-687 (1929).

[20] *Loc. cit.*

From the results of the present work, it is interesting to note that there is a close agreement between theoretical and observed values. But, in the case of the other minerals in which similar halos develop, the agreement does not seem to be satisfactory. The great sensitiveness of cordierite to α-radiation, to which Mügge[21] and Joly and Fletcher[22] have referred, together with the fact that the particular occurrence which we have studied is rich in radioactive material, have combined to yield a profusion of excellent halos in various stages of development—from " embryonic " to " giant."

It has been estimated by several workers that the frequency of the long range α-particles to the normal ones is of the order of 1 : 11,000[23] (see Table I). Evidently therefore, the " giants " cannot be expected to develop unless the nucleus is sufficiently rich in radioactive material, and the radiations have acted for a sufficient length of time to leave their impress on a favourable mineral medium. In the present case, the abundance of halos testifies to the richness of the radioactive material and the lapse of ages since the Archaean —the cordierite-bearing rocks being of Archaean age—has contributed to the long time necessary for the full development of the halos.

In conclusion we wish to express our sincere thanks to Prof. Sir C. V. Raman, Kt., F.R.S., for affording us laboratory facilities and for his kind interest in the work.

210, Bowbazar Street, Calcutta. *14th October, 1930.*

[21] Centralbl. f. Min., (1900), pp. 67-68.

[22] *Loc. cit.*, p. 635.

[23] See Hevesy and Paneth, " Radioactivity," p. 21, Oxford, 1926.

TABLE I.

Long Ranges of α-particles from U and Th Series.

Observer.		Radium C.				Thorium C.				
		Normal.	r_1	r_2	r_3	Normal.	r_1	r_2	r_3	r_4
Rutherford and Wood, 1916.	a						10·2	11·3		
	b					30,000	1	2		
Rutherford 1919.	a		9·0							
	b									
Rutherford and Chadwick, 1924.	a		9·3	11.2						
	b		6	1						
Bates and Rogers, 1924.	a	7.0	9·3	11·2	13·3	8·6		11·5	15·0	18·4
	b	10^6	38	12·5	6·4	10^6		220	47	55
Yamada, 1925.	a		9·3					11·5		
	b									
Meitner and Freitag, 1926.	a						9·5	11·5		
	b									
Philipp and Donat, 1929.	a		9·2	11	11					
	b	10^6	29	4	0·5					
Nimmo and Feather, 1929.	a		9·16				9·9	11·7		

(a) Range in cms. in air at 15°C and 760 mm. pressure.

(b) Relative frequency of the α-particles for the above ranges.

TABLE II.

Uranium Halos. (Theoretical values.)

	NORMAL.								
	Sub-coronal.								
	Embryonic.								
	U i	U ii	Io	Ra	RaEm	RaA	RaC	RaC′	RaF
Range in air in cm. at 15° C.	2·830	2·910	3·194	3·389	4·122	4·722	3·800	6·970	3·925
Range in cordierite in mm.	·01583	·01628	·01786	·01895	·02305	·02641	·02125	·03899	·02196

TABLE III.

Thorium Halos. (Theoretical values.)

	NORMAL.						
	Sub-coronal.						
	Embryonic.						
	Th	RaTh	Thx	ThEm	ThA	ThC	ThC′
Range in air in cm. at 15° C.	2·720	3·870	4·300	5·000	5·700	4·800	8·600
Range in cordierite in mm.	·01522	·02165	·02405	·02997	·03188	·02685	·04810

TABLE IV.

Theoretical Values of Long Range α-particles in Air and in Cordierite.

Range in air in cm. (from Table I).	9·2	9·3	9·5	11·2	11·3	11·5	11·7
Range in cordierite in mm.	·051	·052	·053	·063	·063	·064	·065

TABLE V.

Some Typical (observed) U and Th Normal Halos.

Uranium Halos.					Thorium Halos.					
Description of halo.	r_1	r_2	r_3	r_4	Description of halo.	r_1	r_2	r_3	r_4	r_5
Inner ring grey, middle bleached, and outer yellow.	...	·020	·023	·038	Elliptical nucleus. one half obscured by magnetite.	.015	·019	·028	·032	·047
Circular nucleus: inner ring bleached, outer intense yellow.	·015	...	...	·038	Circular nucleus: grey and yellow rings.	·016	·022	...	·032	...
Inner ring grey, outer rings yellow.	·016	..	·025	·038	Ditto.	...	...	·026	...	·048
Two distinct rings	...	·018	...	·038	Oval nucleus: grey inner and yellow outer rings.	...	...	·024	...	·048
Elliptical nucleus: halo on one side only.	...	·018	...	·038	Halo on one side of the nucleus only.	...	...	·024	...	·048

TABLE VI.

Uranium "Giant" Halos (observed).

Description of Halo.	r_1	r_2	r_3	r_4	r_5
Inner grey, and outer intense yellow	...	...	·023	...	·050
Do. do.	...	...	·023	...	·055
Long narrow nucleus : inner rings bleached, outer intense yellow.	·016	·020	...	·038	·050
Large rectangular nucleus : inner ring grey, second bleached, third light yellow, fourth intense yellow.	·015	·018	...	·037	·050
Nearly rectangular nucleus ...	...	·018	...	...	·050
Large nucleus : grey inner ring, intense yellow outer ring.	...	...	·027	...	·050

TABLE VII.

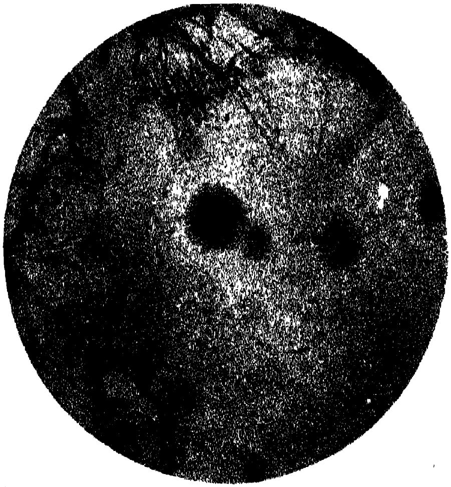
Thorium "Giant" Halos (observed).

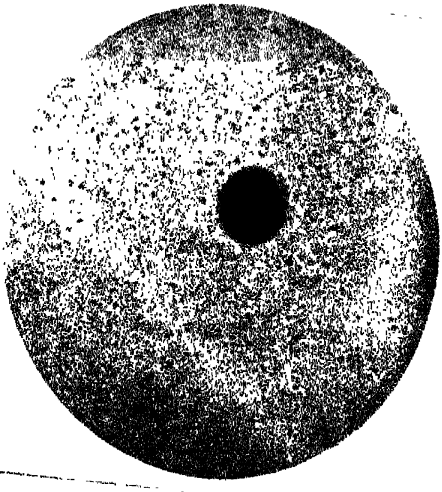
Description of Halo.	r_1	r_2	r_3
arge oval nucleus : inner ring grey, middle bleached, outer intense yellow.	·016	·025	·067
ucleus very small : a single intense yellow ring ...	...	...	·061

EXPLANATION OF PLATE XXVI.

Fig. 1. Uranium halo. (Normal) small nucleus.
Fig. 2. Uranium halo. (Normal) large nucleus.
Fig. 3. Uranium halo. (Giant) large nucleus.
Fig. 4. Thorium halo. (Normal) small nucleus.
Fig. 5. Thorium halo. (Normal) large nucleus.
Fig. 6. Thorium halo. (Giant) large nucleus.
Magnification : 100.

Note.—The very faint outermost rings for figs. 1 and 4 give readings for the U and Th giants respectively.





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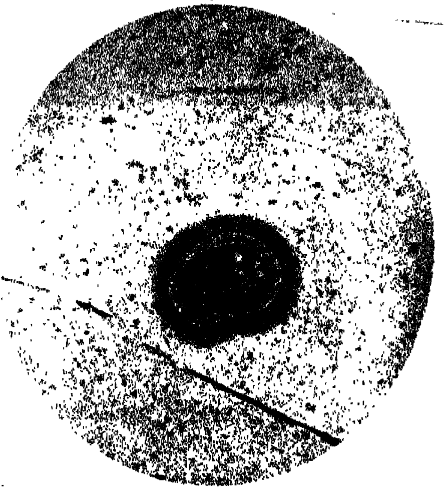

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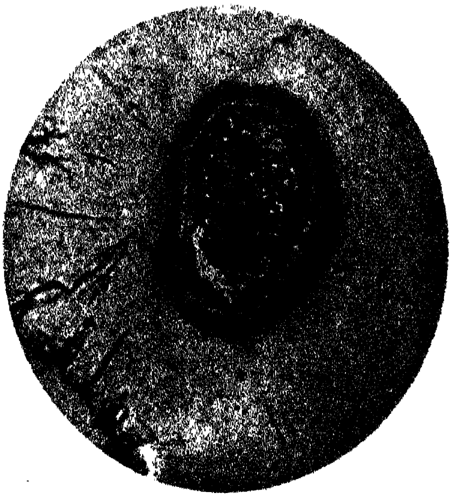

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48

The Frequency of Occurrence of Elements.

By

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Maharajah's College, Jaipur.

(Received for publication, 20th September, 1930.)

Sometime back a scheme was put forward for explaining the formation of elements.[1] From considerations of their atomic weights and atomic numbers, it was suggested that some main groups of elements arise by the syntheses of the rare gases. In each group, one isotope, at least, arose by the combination of two nuclei only, while the majority of the rest included in their formation one or more electrons. The progressingly increasing knowledge of the isotopic weights of the isotopes of elements as given by the mass-spectrograph enables us to form an idea of the energy liberated or absorbed in nuclear synthesis.[2] If the sum of the masses of the components of a nucleus is greater than the mass of the resulting nucleus, the excess of mass gives in its equivalent energy, the amount of energy liberated during the combination. The smoothness of the curve drawn between the packing fractions and the atomic weights enables us to know the packing fraction, and hence the true atomic weight of an isotope, if this is not already known. Thus, for Mg^{24} the packing fraction as given by the curve is most probably $-2·6$; and, therefore, its atomic weight is 23·99376. Hence, the equation of formation can be written,

$$\mathrm{Ne} + \mathrm{He} = \mathrm{Mg} + \Delta m$$
$$20·004 + 4·00216 = 23·99376 + ·0088.$$

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[1] M. F. Soonawala : A Note on the Structure of Atomic Nuclei ; Ind. Journ. Phys., Vol. III, Pt. IV, 1st May, 1929.

[2] F. W. Aston : Nature, 31st December, 1927, p. 956.

By Einstein's Law the energy equivalent to ·0088 atomic weight units is equal to $1·32 \times 10^{-5}$ erg. This amount of energy is radiated out.

Following a similar line of treatment, the value of the energy liberated is calculated for one isotope out of each of the groups of the Table of the previous paper.[1] For the sake of uniformity of treatment, the isotope is chosen for each group which is formed without the introduction of any electrons in addition to the component rare gas nuclei.

We may consider an equation similar to the above to represent a chemical reaction in which $-\Delta H = -\Delta m \times c^2$ is the heat of reaction, where Δm is difference of the masses of the components and the resulting nucleus and c is the velocity of light. We can, then, calculate the change in the free energy of the system before and after the reaction from the relation,

$$\Delta F = \Delta H - T \Delta S.$$

where Δs is the difference in the entropies of the final product and the initial reactants and T the temperature. The entropies concerned in such a case as ours will evidently be those for monatomic gases and will be given by[2]

$$S = k \; ln \left\{ \frac{(2\pi mkT)^{\frac{3N}{2}} V^N e^{5N/2}}{h^{3N} N^N} \right\}.$$

If m_1 and m_2 are the masses of the reacting nuclei and m_3 of the resulting one, then,

$$\Delta S = KN \left[ln \left\{ \frac{h^{3N}}{(2\pi k)^{\frac{3}{2}} e^{\frac{5}{2}}} \right\} - ln \; (T^{\frac{3}{2}} V) + ln \; \left(\frac{m_3}{m_1 m_2} \right)^{\frac{3}{2}} \right].$$

For a temperature of 25°C and one atmosphere pressure, the entropies of monatomic gases are of the order 40 cal./degree per gram-molecule. The origin of the nuclear synthesis can only be guessed. In all probability it is the interior of the stars. Taking as representative values those for the centre of the Sun, a temperature of $1{\cdot}97 \times 10^{7}$°C and pressure $1{\cdot}25 \times 10^{17}$ dynes/cm^2, the entropy of a monatomic gas comes out to be of the order 40 cal./degree once again. To take a typical example, for the reaction,

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[1] l.c., p. 492.

[2] W. H. Rodebush on The Third Law of Thermodynamics in H. S. Taylor's Treatise on Physical Chemistry, Vol. II, p. 1185.

$$A^{40} + Na^{20} = Co^{60}$$

$\Delta S = -2{\cdot}6 \times 10^{-15}$ as averaged per nucleus. In any case, the effect of variations in temperature and pressure seems to be small in calculating entropy differences. From the above, $T\Delta S = -5{\cdot}1 \times 10^{-8}$, on an average per atom, which is seen to be considerably lower in value than the energy of reaction. Hence, the free energy change will be measured almost wholly by the energy of reaction. This is of importance to us as the index of the progress of a reaction in a given sense, a large negative value of ΔF involving a high probability of the reaction proceeding in the corresponding direction, and a positive value of ΔF indicating a very small probability. Thus, ΔF may be taken to measure qualitatively, at least, the relative abundance of the different groups obtained from rare gas syntheses.

Table I shows in its fourth column the energies of reactions per nucleus calculated for the principal typical elements occurring in the scheme of the previous paper. The first column gives the groups or elements typical of each. The second column shows the isotopes for which the reaction energy is calculated. The third column gives the packing fractions calculated from Aston's curve. The fourth column shows the atomic percentage of elements composing the earth as calculated by Clarke.[1] He includes Si with an atomic percentage 9·4; Al, 2·7; Ti, 0·1; Mn, 0·06; and Cr, 0·05; but these fall out of our main scheme. The rare earths are shown in the first column divided into two groups, the first extending from La to Gd, and the second from Tb to Lu; groups which have been recognised as distinct in chemistry and which is also in consonance with our scheme. It can easily be seen that for the alkalis and the halogens, which occupy the first row of our original Table, the energy of formation will be nearly constant though the packing fractions vary widely. Sr and Ba have energies of reaction very near zero, and in their cases the term $T\Delta S$ may be the governing factor for the determination of the free energy changes.

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[1] *Cf.* Miss C. Payne's Stellar Atmospheres, p. 167.

The run of the elements is, at least, in the same direction in the fourth and fifth columns. The alternative process we can conceive of for the formation of a nucleus, that in which A protons combine with A-Z electrons to give a nucleus of atomic weight A and atomic number Z, does not suggest any ready reason why a turning point should occur for the frequency of occurrence in the neighbourhood of the iron group.

TABLE I.

Group.	Isotope.	Packing fraction.	$-\Delta H$	Atomic percentage.
Fe ...	60	−10·0	$+4\cdot7\times10^{-5}$ erg.	46·4
Mg ...	24	−2·6	+1·3 ,,	3·4
Ru ...	108	−6·9	+1·3 ,,	...
Alkalis ...	...	..	+1·2 ,,	·97 − ·4
Halogens ...	...	...	+1·2 ,,	...
Ca .	40	−7·2	+1·1 ,,	1·1
Sr ...	86	−8·2	0 ,,	...
Ba	138	−4·9	0 ,,	...
Rare earths, Group I. ...	158	−8·1	−2·1 ,,	...
Do. do. Group II.	176	−1·4	−11·8 ,,	...

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Reactions at the Surface of Hot Metallic Filaments—Part V.[1]

Thermionic emission and catalytic activity at the surface of hot metallic wires: $H_2 + CO_2 \rightarrow CO + H_2O$ *at the surface of platinum, platinum coated with BaO and thoriated tungsten.*

By

B. S. Srikantan.

(*Received for publication, 7th November, 1930.*)

Abstract.

A semi-qualitative investigation has been made on the emission of electrons from the surfaces of platinum and thoriated tungsten and the minimum temperature at which the thermionic emission is perceptible, has been obtained by extrapolation. This minimum temperature is found to be the same as that required to start the interaction of CO_2 and H_2 on these surfaces. Hydrogen is found to be activated at the same temperature, whilst CO_2 is activated at a lower temperature.

The oxidation of methane at the platinum surface is also shown to be similar.

It is concluded that the activation of gases at a catalyst surface is to a large extent influenced by the capacity of the surface to emit electrons at that temperature.

The phenomenon of surface catalysis greatly depends on the adsorption of the reactants and their consequent activation by the association with the surface. The preceding parts of this paper deal with the kinetics of the interaction of CO_2 and H_2 at various surfaces. The results show the effect of the surface on the reaction and also give us an idea of the relative adsorptive capacities of those surfaces for the gases. But the question how these gases are brought into a reactive state in the presence of a heated catalyst is still left open. The kinetic studies do not help us far in this direction. It appears that in the interpretation of the nature and behaviour of catalysts in gaseous reactions there is some other factor which has not been taken into consideration.

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[1] *Cf.* Parts I-IV, *J. Indian Chem. Soc.*, 1929 (VI), 6, 931, 949, 959; 1930 (VII), 8, 745.

In the course of a discussion on gaseous combustion at the British Association in 1910, Sir J. J. Thomson called attention to the fact that "combustion was concerned not only with the atoms and molecules but also electrons......In reference to the influence of hot surface in promoting combustion...It was not improbable that the emission of charged particles from the surface was a factor of primary importance.........These electrons might produce very important effects by uniting (perhaps selectively) with moisture, with oxygen and with the inflammable constituent of the gaseous mixture ... The action of surfaces might ultimately be found to depend on the fact that they formed a support for layers of electrified gas in which chemical changes proceed with high velocity."[1]

Langmuir[2] found that chemically indifferent gases have no effect on the electron emission from tungsten but catalytic poisons suppressed the emission of electrons from it. Kruger and Taege[3] showed that H_2S, HCN, and CO which are catalytic poisons decreased the photo-electric emission from metals.

Further Thompson[4] finds that thermionic emission is perceptible at a platinum wire, when its temperature is raised to the same temperature at which the union of hydrogen and oxygen begins on the surface. Thompson describes that the influence of excess of oxygen in the mixture is to reduce the temperature of union below that of thermionic emission, whilst the increase of hydrogen in the system does not alter the temperature of union.

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[1] Sir J. J. Thomson, *British Ass. Rep.*, Sheffield, 1910, 501.

[2] Langmuir, *Trans. Farad. Soc.*, 1921, **17**, 641.

[3] Kruger and Taege, *Zeit. Electro-Chem.*, 1915, **21**, 562.

[4] Thompson, *Phy. Zeit.*, 1913, **14**, 11 (*cf.* Kirkby. *Phil. Mag.*, 1905, 10, 476.

While hydrogen is greatly adsorbed by platinum the increase of oxygen in the system would be to displace the hydrogen in preference to oxygen and thus with excess of oxygen the chances of it being adsorbed are greater than that of hydrogen. The reverse is the case with excess of hydrogen.

If it is granted that hydrogen and oxygen must not only be suitably adsorbed but also activated before union, it is evident that the activation of either or both the reactants is brought by the catalyst. The effect of increasing one of the reactants in the mixture shows this. From Thompson's results it follows that at the surface of platinum, oxygen is rendered reactive towards hydrogen at a temperature lower than that at which negative particles are discharged from the surface ; whilst the surface activates hydrogen at the same temperature at which thermionic emission is perceptible.

The results of Thompson in conjunction with those of Langmuir, Kruger and Taege show that the activation of gases at catalytic surface has some connection with the emission of electrons from the surface ; or at least that the activation of hydrogen is in some way influenced by thermal emission from the surface.

The results described in this paper form an attempt to extend the observation of Thompson to the interaction of CO_2 and H_2 at the surfaces of platinum, platinum coated with barium oxide and thoriated tungsten. Since the adsorptive capacity of platinum and that of coated wire for carbon dioxide would vary, it was of great interest to see if the increase of either of the constituents of the reactive gases would influence the temperature at which the reaction commences.

It was also thought interesting to repeat the above experiment with thoriated tungsten wire, since thoriated tungsten is usually preferred to platinum as a suitable substance for giving a source of electrons. The electron emission from thoriated tungsten takes place with great ease at temperatures even far below that required for dull red heat. So experiments were made with CO_2 and H_2 to see if the reaction between them started just at the temperature at which thermionic emission is perceptible as in the case of platinum. Great difficulty was experienced in mounting the wire in the cell with suitable leads. Welding on directly to copper or platinum leads could not be done for the thoriated tungsten easily burns off. After many trials of different methods the following one was found to be workable :

No. 24 copper wire was taken for the leads. A tiny hole was bored along the axis of the wire with No. 80 drill. The clean end of the thoriated tungsten wire was put inside the hole and the wire was pressed in position in a vice, thus forming a good contact. When the wire was stretched along the axis of the tube the two copper leads passed through the glass ends CC (see Fig. 1). The ends CC were closed with molten shellac. But when the reaction was proceeding the cell got appreciably warm and the shellac softened. So it was found necessary to put a water jacket around the cell and water was kept circulating throughout the experiments.

Experimental.

The apparatus used in these experiments is given in Fig. 1. The glass cell D is about 12 cms. in length and 2 cms. in diameter. In general the filament A was welded on to suitable leads CC, which are sealed in the ends of the vessel D so that the wire is stretched in the middle of the cell. It was found that the wire stretched like that at the axis of the tube sagged down a great deal when it was heated and came with in a millimeter or two of the other electrode. So the wire was

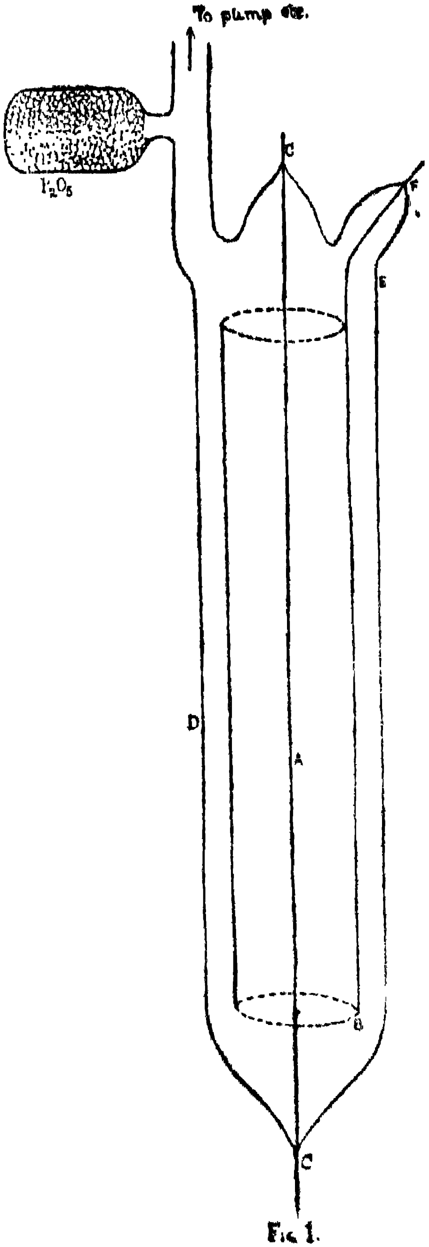

Fig. 1.

twisted into a small spring at one of its ends, and this prevented the two electrodes from coming together. B is a copper foil rolled into a cylinder with a narrow slit, for observation; it forms the positive electrode. A stout copper wire E is soldered on to it, which is in itself welded to a piece of platinum which runs through the glass wall at F.

The cell is connected to a small bulb of P_2O_5 and to a system of pump and manometer. A Geissler tube was connected to the apparatus in order to test the degree of vacuum obtained before an experiment is started. In all the experiments described below the cell was exhausted till no discharge passed through the Geissler tube.

The heating current is supplied by the 110 mains regulated by a system of rheostats. In order to measure the thermionic current the electrode B is connected to the +ive of the high tension batteries (usually 80 volts or 40 volts) through a sensitive galvanometer. The −ive of the high tension is connected on to the −ive of the mains.

Methods of working.

Thermionic emission—The apparatus is first exhausted till no discharge passes through the Geissler tube. The wire was heated by a small current and then the high tension was switched on. Slowly the temperature of the wire was raised. To find out the temperature of the wire, its resistance was noted by means of an ammeter in series and a voltmeter across. So long as the resistance of the wire in any set of experiments was constant, the temperature would be constant. By slowly adjusting the heating current the resistance of the wire was varied. The thermionic current flowing through the galvanometer was noted at various temperatures of wire. In some experiments it was necessary to glow out the wire in vacuum at a high temperature of about 1000°C before consistent readings could be obtained. The thermionic current is expressed as deflections on the galvanometer scale, 1 division $=10^{-6}$ amps.

Before each set of experiments described below the apparatus was well exhausted and the filament was glowed out at about 1000°C and care was taken to see that the Geissler tube showed no discharge passing through.

Interaction of CO_2 and H_2—In these experiments that part of the apparatus used for measuring thermionic current was cut off; only the main heating circuit with ammeter and voltmeter being used. Pure dry CO_2 and H_2 (as in the previous experiments) were let into the exhausted apparatus at suitable pressures. A small heating current was put on for 15 minutes or 1 hour, according to the rate of reaction at that temperature. The resistance of the wire was noted and maintained steady. The resistance of the wire was kept remarkably steady with the rheostats alone, since the temperature at which the experiments were conducted was low and strong convection currents were not set up in the cell as there was no sudden cooling of the cell (as in the previous experiments) and the cell was of small dimensions. After some time, noted by the watch, the current was switched off; sufficient time was allowed to cool down the gases to the laboratory temperature and the water formed to get absorbed by the P_2O_5. The fall in pressure was noted. It was taken to be proportional to the reaction rate in that interval. Thus the reaction rate of the interaction of CO_2 and H_2 with varying quantities of the gases was noted at various temperatures.

A. Platinum wire 12 cms. long, 0·01 cm. diameter.

The platinum wire used in these experiments is an old sample used in the first experiments of part I of this thesis to study the reaction between CO_2 and H_2.

To find out the temperature at which thermionic emission is just perceptible or commences, curves were drawn for each of the experiments performed with this wire. The logarithms of the resistance were plotted against the galvanometer deflection. These graphs (Fig. 2) were straight lines, at low

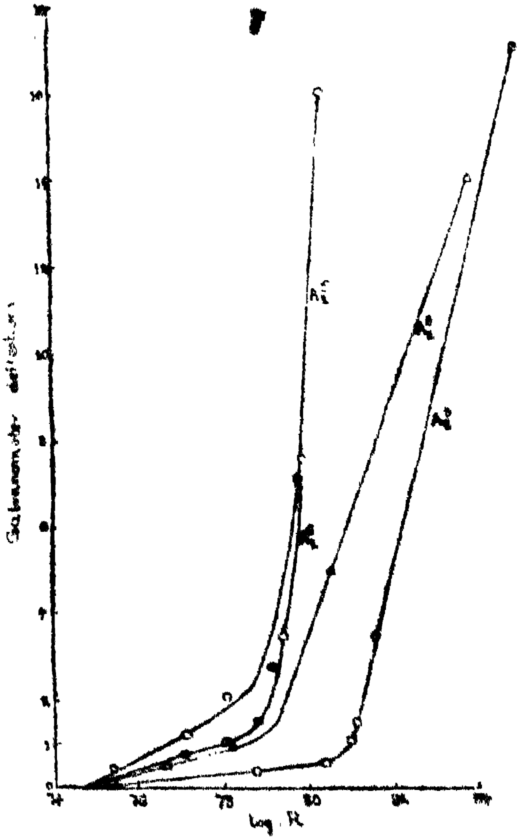

Fig. 2

resistances of the wire, which when produced cut the x-axis sharply; but at higher resistances they suddenly took a bend and went straight almost parallel to the y-axis; this is perhaps due to large currents being set up owing to ionisation due to collision with the residual gases in the tube. On extrapolation for zero thermionic current, these graphs cut the x-axis at a point corresponding to 5·56 ohms. The temperature of the wire corresponding to this is 975° C, calculated from a knowledge of the resistance of the wire at zero degree and its temperature co-efficient.

Experimental data on the kinetics of the interaction of CO_2 and H_2 on this surface are given in Figs. 3 and 4. Extrapolation for zero reaction for experiments A_3 and A_2 gives the resistance of the wire as 5·58 ohms, *i.e.*, at a temperature of 979°C interaction of CO_2 and H_2 begins at the surface of platinum.

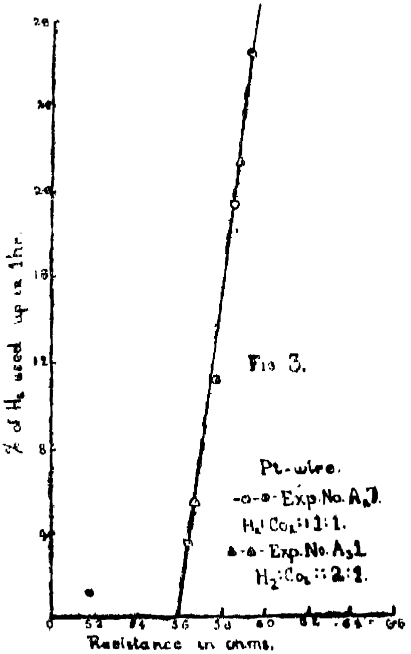

FIG. 3

It is seen that for equimolecular proportions of CO_2 and H_2 (Fig. 3) the reaction begins at the same temperature at which thermionic emission is perceptible and the increase of H_2 in the system does not alter the temperature at which reaction starts. But on plotting data for the resistance and the percentage of the hydrogen used up for Exps. No. A_4 the graph (Fig. 4) does not agree with the previous one. The resistance of the wire when the reaction starts is 3·75 ohms. The temperature at which the reaction starts is 520°C. The increase of CO_2 in the system is to lower the temperature, when the reaction begins, below that at which thermionic emission is perceptible.

It has been shown by Hinshelwood and Prichard[1] that excess of CO_2 in the system actually displaces H_2 from the surface of platinum so that the reaction velocity increases rapidly but after a certain stage the displacement of H_2 is so marked that a further amount of CO_2 actually poisons the wire.

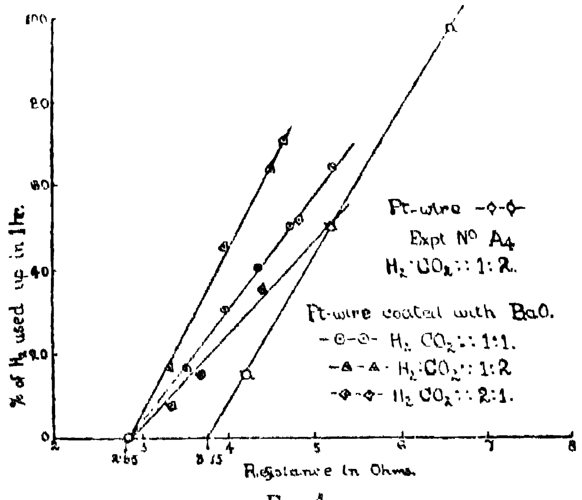

Fig. 4.

So it is obvious that in the interaction of CO_2 and H_2 with stoichiometric proportion of the gases the hydrogen is normally adsorbed on the active centres of the surface and that is activated or rendered reactive at the same temperature at which thermionic emission commences. If displacement of

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[1] Hinshelwood and Prichard, *J. Chem. Soc.*, 1925, 127, 806.

H_2 from the surfaces by CO_2 takes place with excess of CO_2 in the system it has to be concluded that CO_2 is activated at a temperature far lower than that at which thermionic emission is perceptible (*cf.* Thompson).[1]

Note :—In this paper the expression "*the temperature at which thermionic emission is perceptible*" has been used often. It must be understood, however, that it is *not claimed* that below this temperature thermionic emission ceases. Theoretically and practically also sometimes, thermionic emission is possible at low temperatures. In a similar manner catalysis on cold surfaces is also a theoretical possibility. Hence there is an obvious danger in taking the terms literally. All that is claimed is that it is only a condition obtained from the graphs. The similarity of conditions in the two different phenomena is only emphasised.

In Thompson's experiment also, hydrogen was activated at the same temperature at which thermionic emission is perceptible. In order to see if such a result is common only to those reactions concerned with hydrogen as one of the reactants, a few experiments were made to extend this to other reactions. The oxidation of methane by oxygen in the presence of platinum wire was undertaken. The reaction is explosive; so the temperature of the wire was raised very slowly and care was taken to see at each stage if there is any slow combustion taking place. 100 m. m. of each of the gases were put in. As soon as the temperature of the wire reached about 965°C the reaction went off with an explosion and unfortunately the wire snapped off. Considering the explosive nature of the reaction at this temperature the voltmeter and the ammeter readings had to be taken very quickly; so the temperature of the wire noted-965°C-is only approximate; but still it could be taken as fairly agreeing with the previous one.

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[1] Thompson, *loc. cit.*

B. Interaction of CO_2 and H_2 at a platinum surface coated with BaO.

In order to verify the idea that if CO_2 is adsorbed on the surface in presence of H_2, and is activated at a far lower temperature than H_2, it was thought to substitute for platinum a surface which was more conducive to the adsorption of CO_2 than hydrogen. Such a surface was realised in practice by coating the platinum filament with a thin layer of barium oxide, as mentioned before.[1]

On plotting (Fig. 4) as before the resistance and the percentage of H_2 used up in 1 hour it is seen that the least temperature at which the reaction starts is very low and the graphs when extrapolated for zero reaction cut at the same point corresponding to 2·85 ohms. The approximate temperature corresponding to this being 380°C (calculated from a knowledge of the resistance of the wire at zero and its temperature co-efficient of resistance). Since CO_2 is greatly adsorbed by BaO, the increase of H_2 or CO_2 does not alter the temperature of which the reaction starts. However it is far lower than that on the surface of plain platinum.

C. Thoriated Tungsten.

The wire used in these experiments was 10 cms. long and 0·085 m.m. in diameter. The experimental procedure was the same as in the previous case. A great deal of care had to be taken to exhaust the apparatus well for minute amounts of air would oxidise and burn off the wire.

It was seen that a fresh wire gave no thermionic emission even when the filament was heated to visible redness. It is not surprising in view of the fact that a new wire is never so good an emitter as an '*old*' one. So the reaction between CO_2

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[1] Srikantan, *J. Indian Chem. Soc.*, 1929, [VI] 6, 959

and H_2 was first studied and then the wire was used to measure thermionic emission.

Since the temperature coefficient of resistance for this wire was not found out, the temperature at which thermionic emission is perceptible or at which the reaction commences was not calculated. Only the corresponding resistances of the wire were noted. The results are given in the following Tables.

TABLE I.

$CO_2 : H_2 : : 1 : 1.$

Resistance of wire in Ohms ...	16·19	19·57	23·0	25·0
% of H_2 used up in 1 hour ...	*nil.*	*nil.*	10·3	42·8

TABLE II.

+ 80 Volts on plate.

Exp.						
A	Resistance in Ohms. ...	25·31	27·38	30·56	31·47	
	Galvanometer deflections. ...	0·2	0·6	1·0	4·0	
B.	Resistance in Ohms. ...	25·62	27·69	28·48	29·12	29·83
	Galv. deflections. ...	0·2	1·0	1·2	1·9	2·4

On plotting the data from the above Tables it was seen that the thermionic emission was zero or just perceptible when the resistance of the wire was 22·65 ohms. The two values from Table I were on a steep line which cut the axis corresponding to 22·5 ohms. Hence it appears as in the case of platinum that the catalytic reaction between CO_2 and H_2 on the surface of thoriated tungsten commences at the temperature at which thermionic emission is just perceptible.

The few results described above clearly indicate that the activation of gases at a catalyst surface is to a large extent influenced by the capacity of the surface to emit electrons at that temperature.

A few experiments were undertaken to see if the reaction between CO_2 and H_2 would proceed in the presence of a platinum foil and an oxide coated one when exposed to radiations from mercury vapour lamp. 100 m.m. of each gas were taken in a small quartz tube in which about a square centimeter of the platinum foil was suspended. The system was irradiated for 8 hours continuously. The results were negative. Perhaps working at low pressures might be helpful.

D. Further work.

A possible criticism that might be advanced against the experiments described above is that the methods of evacuation adopted are far too inefficient for any measurement of thermionic emission and that the results might have been vitiated by large currents set up due to ionisation by collision. While admitting the validity of such a criticism, it has to be noted that the object of the work was not to make any measurements on thermionic emission *per se*. A qualitative study of the process was only attempted. Further this imperfect evacuation was advantageous inasmuch as the ionisation currents set up, only served to enhance the value of the currents measured and hence render the measurements more sensitive on a comparatively less sensitive instrument.

However, in order to meet the above criticism as far as it lay within the experimental facilities available a thorough evacuation of the apparatus was attempted.

The apparatus was evacuated by means of a Langmuir pump backed by the Topler; and liquid air trap was introduced between the pumps and the cell. Before each experiment the tube was thoroughly baked out at 400°C for 5 hrs.

while the pumps were continuously worked during the whole course of the experiments.

The vacuum obtained was much better than that in the previous experiments. A spiral type of McLeod gauge was used to measure the pressures. Before each set of experiments it was noticed that the apparatus was evacuated to the same degree.

However as measurements of thermionic currents were started it was observed that gases were evolved, perhaps due to the degassing of the anode by the electronic bombardment. This greatly interfered with the measurement of the currents. Therefore the wire was glowed out with 80 volts across the electrodes while the apparatus was baked out as mentioned above.

However it was found advantageous to make measurements, as quickly as possible soon after the procedure described above. The pressures during these experiments were of the order of 10^{-6} m.m. Still it is not claimed that ideal vacuum conditions were attained as in absolute measurements of thermionic currents.

A piece of platinum wire 10 cms. long and 0·01 cm. in diameter was taken for these experiments.

The results show that the conclusions arrived at in the first section of this paper are fully confirmed. In this case the temperature of the wire at which the thermionic emission is perceptible is 770°C, and the temperature at which the reaction between hydrogen and carbon-dioxide is perceptible is 765°C.

This work was done in the laboratories of the Indian Institute of Science, Bangalore, and I take the opportunity of recording my heart-felt thanks to Prof. H. E. Watson for his interest and kind criticism. My thanks are also due to Mr. S. K. Jatkar, M.Sc.

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The Effect of the Indian Mountain Ranges on Air Motion

By

Sudhansu Kumar Banerji, D.Sc.

1. *Introduction.*

In a previous paper,[1] I have discussed in broad outlines without entering into mathematical details, the effect of the Indian mountain ranges during the monsoon months on the configuration of the sea-level isobars which were taken to represent approximately the stream lines in the air at the level of 0·5 km., except very near the mountains. The mountain ranges were assumed to be a series of idealised barriers, namely, vertical walls as shown in fig. 3 of the paper (reproduced in this paper as Fig. 1). The Western Ghats were regarded as an obstacle submerged in the monsoon current and to have a uniform height of 4,000 feet. The other barriers were assumed to be of great height and therefore insurmountable by the monsoon current. The Himalayan Ranges were assumed to have formed with the Burma Hills a rectangular corner over North-east India and with the North-west Frontier mountain ranges another rectangular corner over North-west India. The rest of the surface of India was taken to be at the sea-level.

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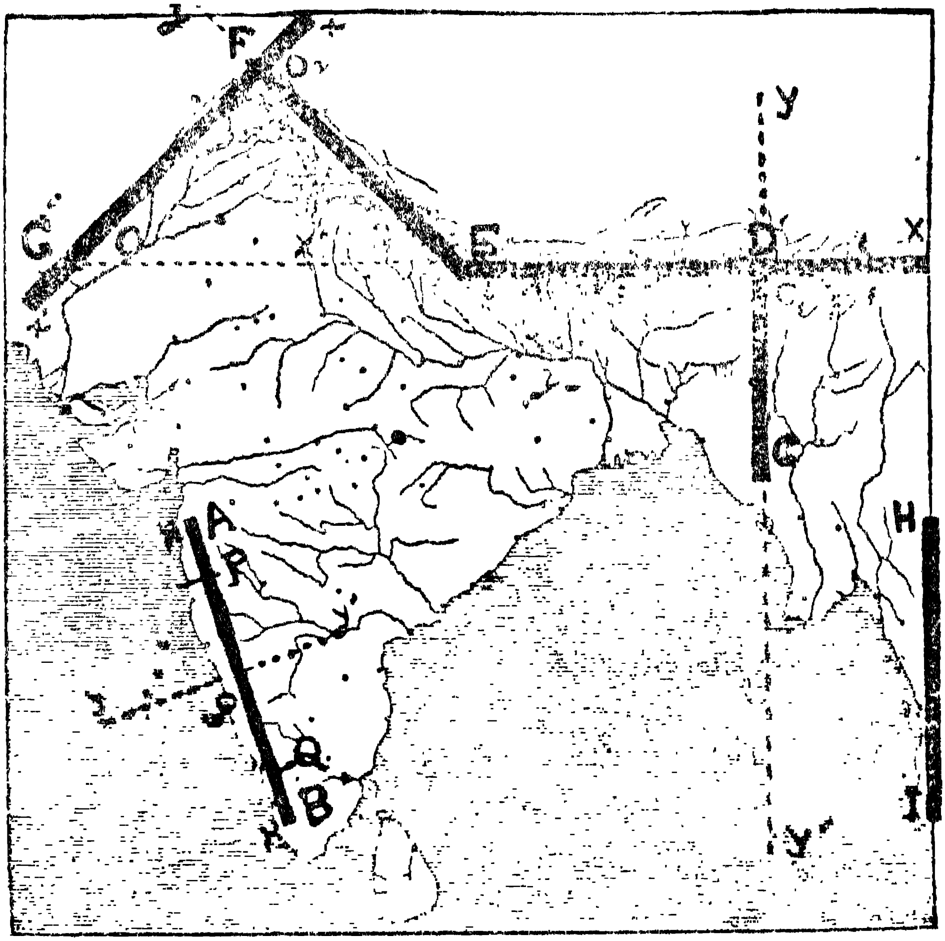
[1] Effect of the Indian Mountain Ranges on the Configuration of the Isobars, *Ind. Journ. of Physics*, Vol. IV, Part VI, pp. 477-502. In the text this paper will be referred to as the first paper.

The air current represented what would be obtained by averaging the motion at a particular instant (8 hrs.) over many years, and all singularities, which might produce strong vertical motion, such as, condensation, thunderstorms, revolving storms, cyclones, etc., were ignored. With all these simplified assumptions, it was shown in the paper that the *peculiarities* in the configuration of the normal monsoon isobars were due to a considerable extent to the influence of the mountain ranges.

It is proposed in this paper to enter into a more detailed analysis of the various points that were only briefly discussed in the first paper.



(Showing the idealised mountain barriers.)

Fig. 1.

2. *How to Determine the Influence of the Mountain Ranges on Air Motion.*

It is important at the outset to form a very clear conception of the manner in which we can determine the influence of the mountain ranges on the air motion. We must first know the motion when the mountain ranges are all absent and then find out how the motion will be modified when the mountain ranges are brought in.

Air motion in the atmosphere can be traced to the two equally important factors:—

(1) That the atmosphere forms a huge and complex thermodynamical engine.

(2) That the earth is rotating round its axis.

Now let us consider the following two states:—

(1) There are no mountains and the earth is a perfectly spherical ball rotating round its axis.

(2) The earth is a perfectly spherical ball rotating round its axis but all the important mountain ranges stand as walls of equivalent heights normal to its surface.

If we assume that in both the states the absorption and the radiation of the surface of the earth are substantially the same, then the thermodynamical mechanism is equally operative in both the cases for the production and maintenance of wind. There will, however, be an important difference in the two states in regard to the influence of the earth's rotation on the lower layers of the atmosphere. In the first state, as the earth rotates, the frictional force will be communicated to the air by its spherical surface. Consequently relative motion of a certain type will be set up in the layer of air next to the ground. In the second state, the air in the lower atmosphere will be confined in more or less partially closed spaces and as the earth rotates, the vertical walls will not only act as constraints to the relative motion in the air introduced by the rotation of its spherical surface but also to the air currents generated by the thermodynamic factors. If, then, we wish to form a combined picture of stream lines in the air, we must in the first instance form two separate pictures as follows:—

(1) A picture of stream lines, which will be produced by the thermodynamical mechanism alone, assuming that the earth has a perfect spherical shape and is rotating round its axis with uniform velocity.

(2) A picture of stream lines, which will be produced by the mountain barriers alone, assuming that the thermodynamical mechanism is absent, and the stream lines are due purely to the relative motion introduced in the air on account of the presence of the barriers on the rotating earth.

These will be referred to as Field No. 1 and Field No. 2 respectively. It need hardly be mentioned that in nature we can never visualise Field No. 2. For, nowhere can the thermodynamical factors be absent.

Since in both the fields, the earth is supposed to be uniformly rotating round its axis, they are mutually compoundable, and since Field No. 1 represents the primary current and Field No. 2 the disturbance due to the boundaries, a good approximation will be obtained of the combined field if these two component fields are compounded together. When, however, a closer approximation is desired it will be necessary to calculate the smaller order terms involving the mutual action of these two fields.

Owing to the complexity of the phenomena it is almost impossible to discuss the problem for the world as a whole even under the most simplified assumptions. We will therefore confine the investigation to the special case which is the subject-matter of this paper, namely, the influence of the Indian mountain ranges on the monsoon current.

When dealing with any small area on the earth's surface, the earth's rotation will be mathematically equivalent to taking the area as rotating round an axis through its mean point normal to its surface with an angular velocity $\omega \sin \phi$, where ω is the angular velocity of the earth and ϕ the latitude of the mean point. India with its mountain ranges is thus equivalent to a rotating frame in the atmosphere.

Let us now discuss Field No. 1 during the south-west monsoon. When the mountain ranges are absent the air motion over the country is due entirely to (1) the thermodynamical mechanism which produces and maintains the monsoon current, (2) the earth's rotation, and (3) the friction communicated by the spherical surface of the earth. It is not the object of this paper to enter into the details of this mechanism, but, we note that the air motion is controlled mainly by the pressure gradient introduced by the permanent high pressure region in the south Indian Ocean and the seasonal low pressure with its core covering a wide region extending from North-west India to North Africa, directed by the earth's rotation. Besides, the surface friction will influence the air motion in the lowest stratum up to a height of 0·3 km. to 0·5 km.

Why should there be a permanent high pressure region in the south Indian Ocean? What determines the magnitude of the central pressure and the location of the anticyclone? These are questions for which we have at present no satisfactory answer. We are, however, not concerned with these questions in our present discussion, but we are concerned with the dimensions, intensity and the location of the 'Low' over Central Asia. For, this low pressure region is so near India that it mainly controls the air current over the country. The pressure over this region is not permanently 'low.' It is 'high' during winter and 'low' during summer. That heat plays a considerable part in determining the pressure over this region is obvious. But, *if heat was the only cause of the development of the 'Low' in summer, why does the area of lowest pressure in this extensive low pressure region lie over Sind or its neighbourhood instead of over the Sahara desert?* Do the Himalayan Range, and the mountain ranges of the North-west

Frontier and Central Asia play any part in displacing the area of lowest pressure from the Sahara side towards India? One of the most important points which I emphasised in the first paper is that these mountain ranges have a tendency to set up closed stream lines in the air. We shall discuss this point in considerable detail in this paper. It should, however, be noted here that if we have reasons to think that the rectangular corner formed by the Himalayan Range and the mountains of the North-west Frontier has a considerable influence in determining the position of the area of lowest pressure over Sind, we have no right to take the 'centre' of the 'Low' to be over Sind while determining the air current in Field No. 1, because this field completely ignores the existence of mountain ranges. We must take the centre of the 'Low' to be somewhere near the central part of the low pressure area extending from North-west India to North Africa.

The air circulation in Field No. 1 under the influence of the 'High' and 'Low' mentioned above coupled with the earth's rotation consists therefore of the monsoon current moving in a great sweep over India round the centre of the 'Low.' The current has probably a thickness of 4 to 5 km. It generally converges towards the low pressure region and as a direct consequence of the earth's rotation the direction of motion round it is anti-clockwise. Above this layer of monsoon current there is a divergent current circulating round the low pressure in some direction opposite to that of the monsoon current. Such then is the circulation which constitutes Field No. 1. To fix our ideas, let us obtain mathematical expressions for this field. This is possible under very definite assumptions. As in the first paper we assume:—

(1) *A steady circulation.*

The representative map for this circulation is not what will be given by a single 8 hrs. weather chart on any day during the monsoon months, but what will be given by averaging the motion at this hour during the monsoon months for many years. We shall take the normal maps given in the *Climatological Atlas of India* as the nearest approach to such maps.

(2) *The vertical motion everywhere is negligibly small compared with the horizontal motion.*

This assumption is not rigorously true everywhere over India. But, in view of the fact that the monsoon air has been taken to represent average conditions, and the surface of the country is supposed to be in the mean sea level in the field under consideration, the assumption is very approximately true except in the neighbourhood of the centre of the 'Low,' where vertical motion must exist. On this assumption, we can treat the motion on each horizontal plane independently and therefore consider it to be two-dimensional and expressible in the form

$$\left.\begin{aligned} \frac{\partial u}{\partial t}+u\frac{\partial u}{\partial x}+v\frac{\partial u}{\partial y}&=X-\frac{1}{\rho}\frac{\partial p}{\partial x},\\ \frac{\partial v}{\partial t}+u\frac{\partial v}{\partial x}+v\frac{\partial v}{\partial y}&=Y-\frac{1}{\rho}\frac{\partial p}{\partial y},\end{aligned}\right\} \tag{1}$$

where the positive direction of x-axis is towards east and that of y-axis towards north, (u, v) are the components of velocity at the point (x, y), p is the pressure, ρ the density of air and X, Y express the combined influence of the rotation of the earth and of friction.

The consideration of the earth's rotation necessitates the introduction of a force whose components are

$$X_1=-\lambda v, \qquad Y_1=+\lambda u, \tag{2}$$

where $\lambda=2\omega\sin\phi$.

It is to be noted that when the force due to earth's rotation is introduced into the equations in this form, the axes of co-ordinates may be regarded as fixed axes in space.

The friction is sensible only near the ground surface up to the height of 0·3 km. to 0·5 km. and within this region it introduces the components

$$X_2 = -ku, \qquad Y_2 = -kv, \tag{3}$$

where k is a frictional constant, which is dependent on the nature of the earth's surface and decreases with height. Moreover, for steady motion,

$$\frac{\partial u}{\partial t} = \frac{\partial v}{\partial t} = 0. \tag{4}$$

The equations therefore reduce to the form

$$\left.\begin{aligned} \frac{\partial P}{\partial x} + ku &= -(\lambda + \zeta)v \\ \frac{\partial P}{\partial y} + kv &= +(\lambda + \zeta)u \end{aligned}\right\} \tag{5}$$

where $$P = \frac{p}{\rho} + \tfrac{1}{2}(u^2 + v^2),\ \zeta = \frac{\partial u}{\partial y} - \frac{\partial v}{\partial x}. \tag{6}$$

Oberbeck[1] has shown that for purely horizontal motion $\zeta = 0$ and the solution of the above equations can be expressed in the form

$$u = \frac{\partial \psi}{\partial x} - \frac{\lambda}{k}\frac{\partial \psi}{\partial y},\ v = \frac{\partial \psi}{\partial y} - \frac{\lambda}{k}\frac{\partial \psi}{\partial x}, \tag{7}$$

where $\nabla^2\psi = 0$. The stream lines near the ground surface are given by an expression of the form

$$\Phi - \frac{\lambda}{k}\psi = 0, \tag{8}$$

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[1] The movements of the Atmosphere on the Earth's Surface, Wiedemann's Annalen der Physik und Chemie, 1882, Vol. XVII, pp. 128-148.

where ψ and Φ are two orthogonal functions related in the form

$$\Phi + i\psi = F(x + iy). \tag{9}$$

The stream lines thus intersect the system of lines given by $\psi = const.$ at an angle that is everywhere the same. If we designate by ϵ the angle that the direction of the wind makes with the normal to the curves $\psi = constant$, we have

$$\tan \epsilon = \frac{\lambda}{k}. \tag{10}$$

When k becomes negligible, that is to say, above 0·5 km., the direction of the wind will coincide with the curves $\psi = constant$. In other words, $\psi = \text{const.}$ will represent the stream lines above this level.

Now, let us take the origin in the centre of the 'Low' over Central Asia as shown in Fig. 2, and use polar co-ordinates. In the free air the isobars are approximately a series of concentric circles and therefore, the stream lines are represented by the equation

$$\psi = \log r. \tag{11}$$

The orthogonal function, corresponding to this form of ψ, is $\Phi = \theta$. Consequently the stream lines near the ground surface have the form

$$\theta - \frac{\lambda}{k} \log r = \text{constant}. \tag{12}$$

These are a series of logarithmic spirals having their poles at the centre of the 'Low.'

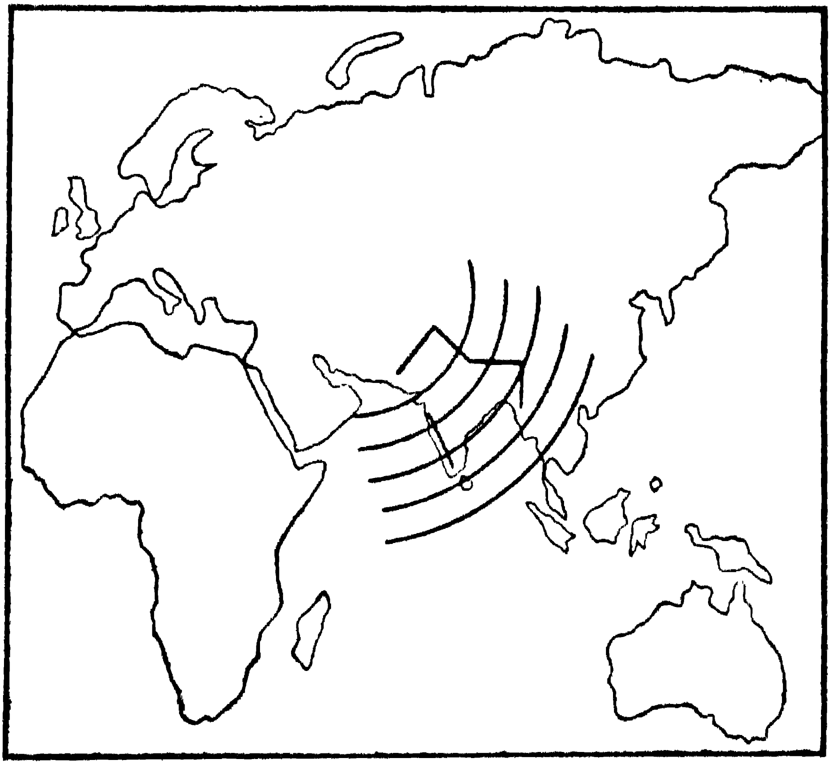

Fig. 2.

In one of the charts which accompanied his "Dynamic Meteorology and Hydrography" Bjerknes has drawn the stream lines over India near the ground surface from the observed normal directions of wind in July. This chart therefore presents important observational materials. The essential features of this chart have been reproduced in Fig. 3. As this chart represents actual conditions taking account of the topography of India as it is, it is really a projection of the stream lines in three dimensional space[1] on a horizontal plane. In the diagram, therefore, the stream lines meet

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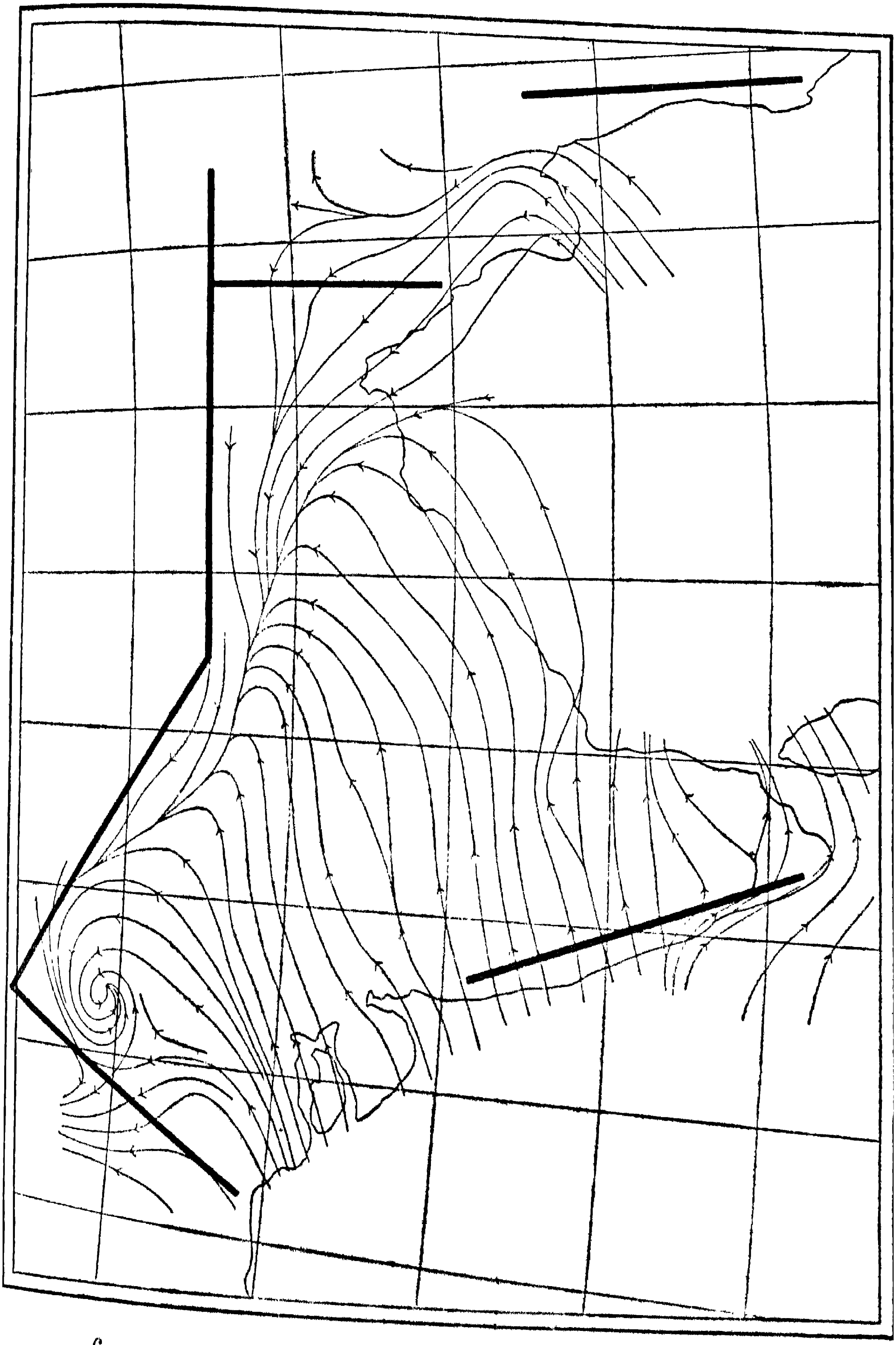
[1] If Dr. Simpson has drawn his diagram of stream lines (Fig. 4, Quart. Journ. Roy. Met. Soc., Vol. XLVII, p. 152, 1921), in this sense, then his drawing will not offend against any hydrodynamical principles. But there are important differences between his drawing and Bjerknes' drawing.



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each other at many places. The point of great interest however is the manner in which the stream lines meet at the centre of the 'Low' over North-west India in the shape of logarithmic spirals, agreeing with the theoretical results given above. We shall discuss the other features of this map elsewhere in this paper.

We thus see from the preceding discussion that at 0·5 km. level and aloft up to a height, within which we can assume the existence of a steady monsoon current under average conditions, the stream lines will be approximately a series of circles given by

$$\psi = \log r,$$

the centres of the circles being in the centre of the extensive low pressure region extending from North-west India to North Africa. It will be seen from Fig. 2 that over the Indian area these circles are practically straight lines. They can therefore be expressed, as was done in the first paper, by the approximate equation

$$\psi = \mathrm{V}x - \mathrm{U}y \qquad \dots \quad (13)$$

3. *Relative Motion in the Air produced by Mountain Ranges.*

We shall now proceed to discuss Field No. 2, namely, the field of stream lines which will be produced by the mountain barriers alone. The mountain barriers along with the surface of the ground, on which they stand as vertical walls, must, as already explained, be regarded as a rotating frame, rotating with an angular velocity $\omega \sin \phi$, where ϕ is the mean latitude of the area concerned. Since we are now considering purely horizontal motion, it is clear that the relative motion, which will be introduced in the air as a result of the additional constraints formed by the barriers, will be limited in the neighbourhood of the barriers, and will extend from the ground surface up to a height equivalent to the mean height of the barriers. The relative motion arises on account of the fact that the fluid in motion has to satisfy—

(1) certain equations at the barriers (boundary conditions), and

(2) different equations at all other points in the fluid (equations of motion).

This is true whether the fluid is regarded as perfect or viscous, although the boundary conditions and the equations of motion are different in the two cases. In the present paper we shall be considering mainly stream line motion and for this type of motion, viscosity of air has almost neligible effect. For, Helmholtz[1] showed many years ago that if air was set in motion and left to viscosity to destroy it, it will take 43,000 years to reduce the motion to half its original value. His computation shows that except near the ground surface, the effects of viscosity are unimportant. These results are based on the ordinary co-efficient of viscosity for stream line motion and are in striking disaccord with experience. Nevertheless, all experiments and observations show that the co-efficient of viscosity for stream line motion is negligibly small compared with that for eddy motion. That viscosity is small for stream line motion can also be seen from the 'gradient equation.' In deducing this equation we neglect viscosity, but it fits in fairly well with the observed isobars. We will, therefore, neglect viscosity.

As a specific example, let us now consider what happens in the rectangular corner over Assam formed by the Himalayan Range and the Burma Hills (Fig. 1). We can consider this as a frame rotating with an angular velocity $\omega \sin \phi$ about a vertical axis through D (Fig. 1), where ϕ is the latitude of the point D. For purely horizontal motions, the stream function ψ must satisfy the condition

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[1] Sitzungsberichte of the Royal Prussian Academy of Science at Berlin, 1888, pp. 647-663.

$$\frac{\partial \psi}{\partial s} = \omega\, r \sin \phi \frac{\partial r}{\partial s} \quad \text{—} \quad (14)$$

at the barrier, where r denotes radius vector from D and δs an element of horizontal length of the barrier.

At any other point in the fluid the stream function ψ must satisfy the equation

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = 0 \quad \ldots \quad (15)$$

It is important to realise that to the function ψ, which satisfies equation (15) consistent with the condition (14), we can add, without in any way vitiating this condition, the solution for the *free* or the *forced* motion assuming that the frame had remained stationary. The reason is that for such motion ψ satisfies the same equation (15), but the boundary condition becomes

$$\frac{\partial \psi}{\partial s} = 0 \quad \ldots \quad (16)$$

This enables us to compound directly the field produced by the barriers and that produced by Field No. 1 impinging on the barriers. For, let

ψ_1 = the stream function due to the barriers, satisfying equations (14) and (15),

ψ_2 = the stream function due to Field No. 1 impinging on the barriers. By ψ_2 we mean the field which will be produced on account of the monsoon current as contemplated in Field No. 1 *flowing past the barriers* assumed to have remained stationary relatively to the current.

Then both ψ_1 and ψ_2 satisfy equation (15), but ψ_1 satisfies the boundary condition (14) and ψ_2 the boundary condition (16). Therefore the stream function ψ for the combined field, namely,

$$\psi = \psi_1 + \psi_2$$

satisfies the boundary condition (14), since

$$\frac{\partial\psi}{\partial s}=\frac{\partial\psi_1}{\partial s}+\frac{\partial\psi_2}{\partial s}=\frac{\partial\psi_1}{\partial s}=\omega\, r\, \sin\phi\,\frac{\partial r}{\partial s}.$$

It is thus clear that the stream function for the combined field must satisfy the boundary condition for a rotating frame.

4. *Field of Stream Lines due to a corner formed by two Mountain Ranges.*

In Fig. 1, the Himalayan Range is shown to form with the Burma Hills a corner over Assam and with the North-west Frontier mountains another corner over North-west India. It is therefore important to know the field of stream lines due to such a corner.

In the first paper the stream function ψ for the *combined field* over the rectangular corner over Assam was expressed in the form

$$\psi=\mathrm{V}r\cos\theta-\mathrm{U}r\sin\theta+\mathrm{A}r^2\cos 2\theta+\mathrm{B}r^2\sin 2\theta+\mathrm{C}r^3\cos 3\theta$$
$$+\mathrm{D}r^3\sin 3\theta+\text{etc.} \qquad \ldots \quad (17)$$

This is a Fourier series satisfying $\nabla^2\psi=0$. Since any continuous function in finite region is capable of being expressed as a Fourier series, this expression is a very general one. Whatever be the solution, it must be capable of being expressed in the above form.

The most important terms of the above solution retained in the first paper were

$$\psi=\mathrm{V}x-\mathrm{U}y+\mathrm{A}(x^2-y^2)+2\mathrm{B}xy,$$

where the axes have their origin at D and are as shown in Fig. 1.

We will now give a proof why these are the most important terms. In determining the field of stream lines due to the rectangular corner over Assam, one has necessarily to bear in mind that this corner is rotating in the atmosphere with an angular velocity $\omega\sin\phi$, where ϕ is the mean latitude, say about 26°. The angular velocity is about 0·44 ω, and is therefore appreciable.

We need not restrict ourselves to the assumption that the corner formed by the two mountain barriers is equal to a right angle. In nature it is never exactly equal to a right angle. We will start with the well-known solution for a rotating circular sector given by Stokes many years ago. If the circular sector be of radius a and angle 2α, the axis of rotation being through the centre (Fig. 4), then Stokes' solution [1] is expressed in the form

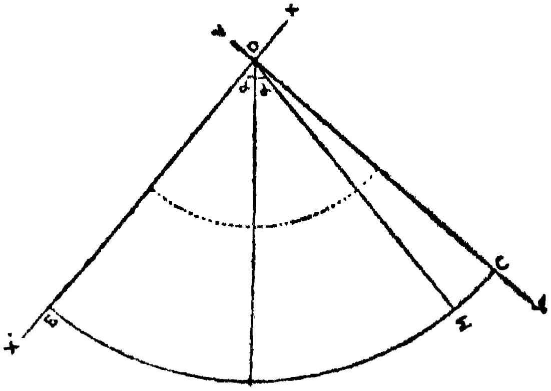

Fig. 4.

$$\psi=\frac{1}{2}\,\omega' r^2\frac{\cos 2\theta}{\cos 2\alpha}+\omega' a^2\sum_0^\infty A_{2n+1}\left(\frac{r}{a}\right)^{(2n+1)\frac{\pi}{2\alpha}}\cos\,(2n+1)\,\frac{\pi\theta}{2\alpha} \tag{19}$$

where

$$A_{2n+1}=(-1)^{n+1}\left\{\frac{1}{(2n+1)\,\pi-4\alpha}-\frac{2}{(2n+1)\pi}+\frac{1}{(2n+1)\pi+4\alpha}\right\} \tag{20}$$

and $\omega'=\omega\sin\phi$, ω being the earth's angular velocity.

In this formula, the middle radius, namely DL, is taken as the initial line from which θ is measured. If we measure θ from the end radius DE then we have to write $\theta-\alpha$ in place of θ in the above formula and we get

$$\psi=\frac{1}{2}\,\omega' r^2\,\frac{\cos 2(\theta-\alpha)}{\cos 2\alpha}+\omega' a^2\sum_0^\infty A_{2n+1}\left(\frac{r}{a}\right)^{(2n+1)\frac{\pi}{2\alpha}}\cos\,(2n+1)\cdot\frac{\pi(\theta-\alpha)}{2\alpha}.$$

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[1] Lamb's Hydrodynamics, fourth edition, p. 84.

If we put $\alpha=\frac{\pi}{4}$, we get the solution for a rectange bounded by the circle $r=a$. But we notice that when we make $\alpha=\frac{\pi}{4}$, cos 2α becomes zero, and therefore the first term in the above solution becomes infinite. But although the first term becomes infinite, the solution as a whole remains finite. We need not, however, consider this case. We shall not make $\alpha=\frac{\pi}{4}$, but slightly less or greater than $\frac{\pi}{4}$, that is to say, we shall write

$$2\bar{a}=\frac{\pi}{2}-\epsilon \qquad \ldots \qquad \ldots \qquad \ldots \qquad (21)$$

where ϵ is a small angle, positive or negative.

We will consider a to be very large and determine the stream function in the region close to the origin. This will be equivalent to regarding r/a to be very small. If, therefore, in the series

$$\omega' a^2 \sum_0^\infty A_{2n+1} \left(\frac{r}{a}\right)^{(2n+1)\frac{\pi}{2\alpha}} \cos (2n+1)\frac{\pi(\theta-\alpha)}{2\alpha},$$

we neglect all terms involving powers of r/a greater than 2, it reduces to the first term only, namely,

$$A_1\omega' r^2 \cos\frac{\pi(\theta-\alpha)}{2\alpha},$$

$$\text{where } A_1=-\frac{1}{2\epsilon}+\frac{2}{\pi}-\frac{1}{2\pi-2\epsilon} \qquad \ldots \qquad \ldots \qquad \ldots \qquad (22)$$

we thus get

$$\psi=\frac{1}{2}\omega' r^2\frac{\cos 2(\theta-\alpha)}{\cos 2\alpha}+A_1\omega' r^2\cos\frac{\pi(\theta-\alpha)}{2\alpha}$$

approximately.

Putting now $2\alpha=\frac{\pi}{2}-\epsilon$, we get

$$\psi=\frac{1}{2}\omega' r^2\frac{\sin(2\theta+\epsilon)}{\sin\epsilon}+A_1\omega' r^2\cos 2\left(\theta-\frac{\pi}{4}+\frac{\epsilon}{2}\right)$$

$$=\frac{1}{2}\omega' r^2\left\{\cos 2\theta+\cot\epsilon\sin 2\theta\right\}+A_1\omega' r^2\sin(2\theta+\epsilon)$$

$$=\omega'\left\{\frac{1}{2}+A_1\sin\epsilon\right\}r^2\cos 2\theta+\omega'\left\{\frac{1}{2}\cot\epsilon+A_1\cos\epsilon\right\}r^2\sin 2\theta$$

$$= \omega'\left\{\frac{1}{2} + A_1 \sin\epsilon\right\}(x^2 - y^2) + \omega'\left\{\frac{1}{2}\cot\epsilon + A_1\cos\epsilon\right\}.\ 2xy$$

$$= A(x^2 - y^2) + 2Bxy,$$

where

$$A = \omega'\left\{\frac{1}{2} + A_1 \sin\epsilon\right\},$$

$$B = \omega'\left\{\frac{1}{2}\cot\epsilon + A_1\cos\epsilon\right\}.$$

The stream function representing field No. 2 due to a rotating corner has therefore the form $\psi = A(x^2 - y^2) + 2Bxy$. As a special case, if we make ϵ *very small*, so that $\sin\epsilon = \epsilon$ and $\cos\epsilon = 1$, we get, by substituting the value of A_1 from (22),

$$A = \frac{3\epsilon}{\pi}\,\omega', \qquad B = \left\{\frac{3}{2\pi} - \frac{\epsilon}{2\pi^2}\right\}\omega'.$$

It will thus be seen that A is considerably smaller than B.

It will be seen also that when ϵ is small, the curves,

$$2Bxy = constant,$$

are a series of rectangular hyperbolas having the barriers as asymptotes. The term $2Bxy$ makes $\frac{\partial\psi}{\partial r} = 0$ on both the barriers. This term therefore represents the free motion. The rotation brings in the term $A(x^2 - y^2)$.

A close approximation to the stream function ψ for *the combined field* is obtained by compounding Field No. 1 and Field No. 2. We thus get for the combined field

$$\psi = Vx - Uy + A(x^2 - y^2) + 2Bxy.$$

It will be clear from Stokes' solution that even when the barriers differ from the idealised condition to a minor extent, these will be the most important terms. *This solution gives an instantaneous picture of the stream lines in the air in exactly the same sense as isobars do in a synoptic weather map.*

To understand this analogy, one should remember that the stream lines represented by ψ refer to axes instantaneously fixed in space. The x-axis coincides with the Himalayan Range and the y-axis is perpendicular to it. When the stream lines are drawn over the field at the instant, $t=o$ say, the axes are momentarily at rest. When they are drawn at another instant, $t=t'$, the x-axis still coincides with the Himalayan Range and the y-axis is perpendicular to it and they are again momentarily at rest. The stream lines so drawn therefore represent instantaneous directions of motion with reference to fixed axes. Let us now compare this field with the isobaric field in a synoptic map. The synoptic isobaric field agrees closely with the ' gradient equation ' in free air. In deducing the gradient equation, the deviating force ($2\omega\rho V\sin\phi$) due to earth's rotation is included in the statement of forces acting upon each element of air. The rotation of axes is thus accounted for and the equation therefore refers to fixed axes (' Dictionary of Applied Physics,' Vol. III, p. 28). We thus see that the synoptic isobars also represent instantaneous directions of motion with reference to fixed axes.

The stream lines drawn on the surface of the earth must necessarily refer to fixed axes, for, the word ' direction ' has no meaning when it is referred to a set of rotating axes. Let us now suppose that we have a large number of wind vanes at 0·5 km. *level* distributed all over India and that they are all read at a particular instant (say, 8 hrs.). Each observer reads the direction of the vane with reference to a pre-arranged axis, namely, the north-south line, and at that instant this line remains momentarily fixed in space.[1] If now a series of stream lines be drawn from all these readings, these will be synoptic stream lines with reference to instantaneously fixed axes. Under balanced forces these stream lines will be the same as the sea-level isobars. We can readily understand what such an *instantaneous* picture of stream lines means from the familiar diagrams of stream lines around a circular cylinder moving in an infinite liquid and those in a stream flowing past a fixed cylindrical obstacle. The moving cylinder is equivalent to a moving doublet and *at any instant* the stream lines around it are the same as those around a doublet. If then one sits on the circular section of the cylinder and takes an instantaneous view all round, the stream lines will appear to him exactly like those due to a doublet. If on the other hand, he attaches a flag to a particular element of water and then sits down on the moving cylinder to watch its motion with the march of time, he will find that its path is exactly like one of those stream lines which one would draw in a fluid flowing past a fixed cylindrical obstacle (Lamb's Hydrodynamics, fourth edition, pp. 74-75). It will thus be seen that there will be wide difference between the 'instantaneous picture' and 'time picture' of stream lines around a solid moving in any manner in a fluid, which will be taken by an observer sitting on the solid. An instantaneous picture of this kind will be exactly similar to the one which an air pilot flying low with a horizontal velocity of 200 ft. per sec. will take of moving objects on the surface of the earth by exposing his camera for $10^{-\infty}$ second. Such a picture will be the same as the one which he would have obtained if he had remained stationary at the point where he exposed the camera. The picture, however, would be different if he exposed the camera for 10 seconds while flying. In an instantaneous picture the motion of the observer (or camera) does not count in the least. It is *ipso facto* a picture with reference to momentarily fixed axes.

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[1] To help the mind, the N—S line may be considered to be passing through Polaris and the angles measured on the plane passing through this line instead of on the horizontal plane, for, the angle between any two lines on this plane is equal to the angle between their projections on the horizontal plane. In the usual synoptic map drawn on a plane passing through or parallel to the earth's polar axis, the N—S line always passes through Polaris.

It is important to notice, as explained in the first paper, that the term $2Bxy$ in the stream function has no influence so far as the points of intersection of the stream lines with the barriers are concerned. In the actual drawing of the stream lines in the neighbourhood of the barriers, however, the term $2Bxy$ is of great importance, because B is considerably greater than A. *It will thus be obvious why the theoretical stream lines in free air as drawn in Fig. 8 of the first paper over North-east India and the head of the Bay have the hyperbolic shape corresponding more to the term $2Bxy$ than to the term $A(x^2-y^2)$.* The stream lines as drawn in that figure over this area are really combinations of both these terms as well as $Vx-Uy$. All the deductions made in the first paper from the above formula are therefore justified.

It will be seen from Fig. 8 of the first paper that as a consequence of the above form for the stream function, a large number of stream lines intersect the Himalayan Range. This is so, because the barriers form a rotating frame in the atmosphere. The point as to what happens to the air when more than one stream line intersect a barrier requires consideration. It is important to bear in mind that the instantaneous stream lines relative to the rotating frame do not give the paths of air particles. They merely represent the instantaneous directions of motion. The paths of air particles as time progresses, when determined by the methods[1] used by Prof. Morton, do not intersect the barrier, unless there is 'dead air,' that is to say, air relatively at rest with respect to the barrier. We will further consider this point elsewhere in this paper, when we discuss in detail the air motion close to a barrier.

5. *Why a Corner formed by two Mountain Barriers tends to produce closed Stream Lines.*

One of the most important deductions made in the First paper from the solution given in the preceding article was the formation of closed stream lines round the rectangular corner over North-west India. As a direct consequence of this influence exercised by the mountain barriers on the air motion, the area of lowest pressure in the extensive low pressure region from North-west India to North Africa lies over or in the neighbourhood of Sind and not over Sahara.

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[1] Proc. Roy. Soc. A, Vol. 89, p. 106 (1913).

It is important to realise why a corner formed by two barriers and rotating in a fluid tends to form closed stream lines. Hydrodynamics furnish several beautiful examples for which complete solution has been worked out. In Fig. 5 has been reproduced the stream lines for an elliptic frame rotating steadily round an axis through its centre, given on page 85 of Lamb's Hydrodynamics (fourth edition). These are lines for equidistant values of ψ. It will be seen how the stream lines have become congested in the neighbourhood of the two elongated ends of the ellipse, and how they all form closed curves.

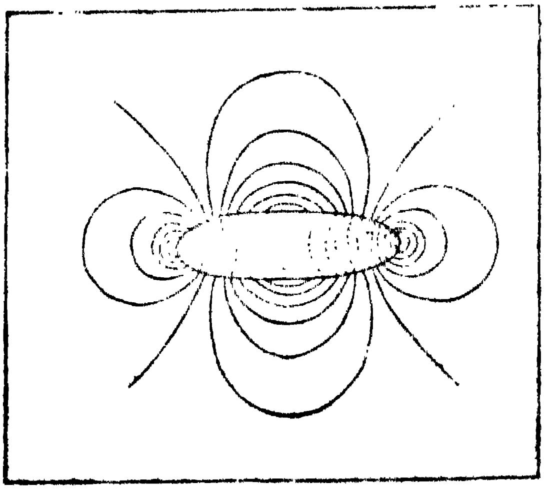

Fig. 5.

I have also given in Figs. 6 (*a*) and 6 (*b*), the diagrams of stream lines for the two undermentioned cases, which were completely solved[1] by Stokes and St. Venant many years ago.

(1) Motion of a fluid inside and outside a vessel in the form of a rectangular prism, when the latter is rotating with a constant angular velocity about an axis parallel to its length and passing through the centre of its section.

(2) Motion of a fluid inside and outside a vessel in the form of an equilateral triangular prism, when the latter is rotating with a constant angular velocity about an axis parallel to its length and passing through the centre of its section.

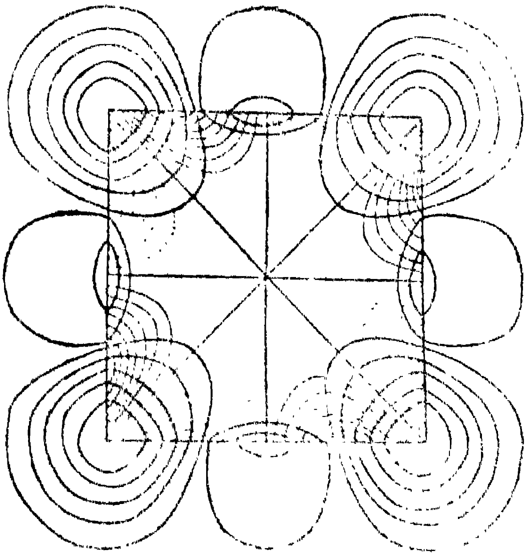

Fig. 6 (a).

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[1] Stokes discussed both these cases as problems in Hydrodynamics, see Scientific Papers, Vol. I, p. 8, also pp. 17-68. St. Venant, however, gave the solutions for these two cases in connection with the analogous problem of 'Torsion.' The functions ϕ and ψ which occur in 'Torsion problems' are exactly identical with the velocity potential and stream function in Hydrodynamics for the motion introduced by rotation of hollow cylinders and prisms, assumed rotating about any axis parallel to their generating lines with an angular velocity—1. The solution for the triangle is given in Lamb's Hydrodynamics, fourth edition, p. 83. The solution for both cases are given on pp. 305-307 of Love's Elasticity, second edition. These solutions, along with many other interesting cases and diagrams, are given in Thomson and Tait's Natural Philosophy, Vol. I, arts. 706-709. It is worth while noticing that in the solution for a rotating rectangle, the important term is x^2-y^2,

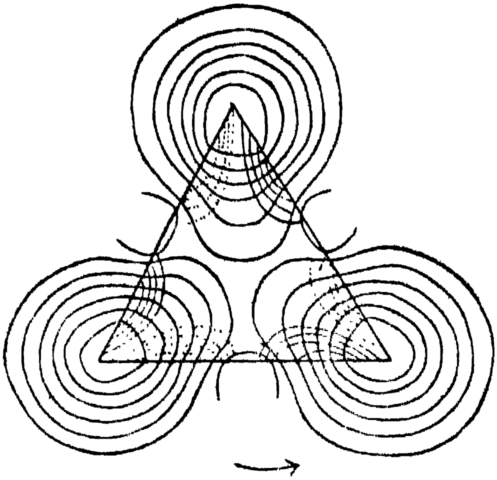

Fig. 6 (b).

These diagrams are completed drawings from St. Venant's original diagrams. St. Venant gave only the equipotential lines, shown by thin lines in the above diagrams. The thick lines, representing the stream lines, have been drawn by me for equidistant values of ψ. Perfect accuracy in drawing the lines has not been attempted, but they are accurate enough for all practical purposes. It will be seen that in these cases also the stream lines become congested round the corners and they all form closed curves. Hydrodynamics abounds in examples of this kind and they all show similar features. A careful study of these cases leaves very little doubt in one's mind that the corner formed by the mountain barriers over North-west India must have a tendency to develop closed stream lines round it and thus help the thermodynamical factors in forming a deep 'Low' over Sind or its neighbourhood.

6. *Stream Lines in the neighbourbood of the Western Ghats.*

The value of the angular velocity in the centre of the Ghats is nearly equal to half its value at any point of the Himalayan Range. The influence of the earth's rotation is therefore considerably less here than in the neighbourhood of the rectangular corner over North-east or over North-west

India. Fig. 4 of the first paper for a current from the north-west impinging on the Ghats was drawn without taking the rotation into account as the formulæ used definitely show. It was prepared for the sake of comparison with the May isobars in the neighbourhood of the Ghats. In this month, the monsoon is not fully established, and the 'Low' over Sind is ill-developed. The current strikes the Ghats more or less from a westerly direction and is apparently very shallow. These conditions therefore represent very nearly the case of a stream flowing past an insurmountable obstacle, and a very close agreement was found between the theoretical and observed stream lines even though rotation was neglected. We shall presently show that in consequence of the low latitude and limited length (about 800 miles) of the Western Ghats, the rotational term will affect the configuration of the stream lines only in the close proximity of the barrier.

In drawing the theoretical stream lines in the neighbourhood of the Western Ghats in Fig. 8 of the first paper due account was taken of the rotation as was done in drawing them in the other parts of the diagram.

If the Western Ghats be assumed to coincide with the x-axis and its edges to lie at the points $x = \pm c$, then the stream function[1] for a current impinging on it, when rotation is taken into account, is

$$\psi = c \sinh \xi \,(\mathrm{U} \sin \eta - \mathrm{V} \cos \eta) + \tfrac{1}{4}\omega' c^2 e^{-2\xi} \cos 2\eta,$$

where $x = c \cosh \xi \cos \eta$, $y = c \sinh \xi \sin \eta$, and $\omega' = 0{\cdot}24\omega$, ω being the earth's angular velocity.

It is easily seen that $e^{-\xi}$ is of the order $1/r$, where r denotes radius vector from the centre of the barrier, and $e^{-2\xi}$ of the order $1/r^2$. Consequently at some distance from the barrier, the term depending on rotation is of considerably less importance compared with the other terms.

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[1] Lamb's Hydrodynamics, fourth edition, p. 81 and also p. 85.

In drawing the stream lines in Fig. 8 of the first paper, the current was considered to impinge on the Western Ghats almost at right angles. In fact it is very nearly so. If rotation was neglected, the stream line, $\psi=0$, would have intersected the barrier at the mid-point, but when rotation is taken into account, it does not do so. We shall, therefore, determine the points of intersection of the stream line $\psi=0$.

When the current impinges at right angles to the barrier, that is to say, x-axis, we have $U=0$, and therefore the stream function becomes

$$\psi=-c\sinh\xi.\ V\cos\eta+\frac{1}{4}\,\omega'\,c^2e^{-2\xi}\cos 2\eta.$$

The stream line $\psi=0$ has therefore the equation

$$V\sinh\xi.\ \cos\eta-\frac{1}{4}\,\omega'\,ce^{-2\xi}\cos 2\eta=0.$$

To find the points of intersection with the barrier we notice that near the barrier $\sinh\xi$ approaches zero, that is to say, $\sinh\xi\longrightarrow 0$. Consequently

$$e^{\xi}-e^{-\xi}\longrightarrow 0,$$

or $$1-e^{-2\xi}\longrightarrow 0.$$

In other words $e^{-2\xi}$ is very nearly equal to unity.

The stream line $\psi=0$ therefore intersects the boundary at the points given by

$$\cos 2\eta=0,$$

or at the four points given by

$$\eta=\frac{\pi}{4},\ \frac{3\pi}{4},\ -\frac{\pi}{4},\ -\frac{3\pi}{4}.$$

Now if AB is the barrier (Fig. 7), the point A ($x=c$) on the barrier corresponds to $\eta=0$ and the point B ($x=-c$) to $\eta=\pi$.

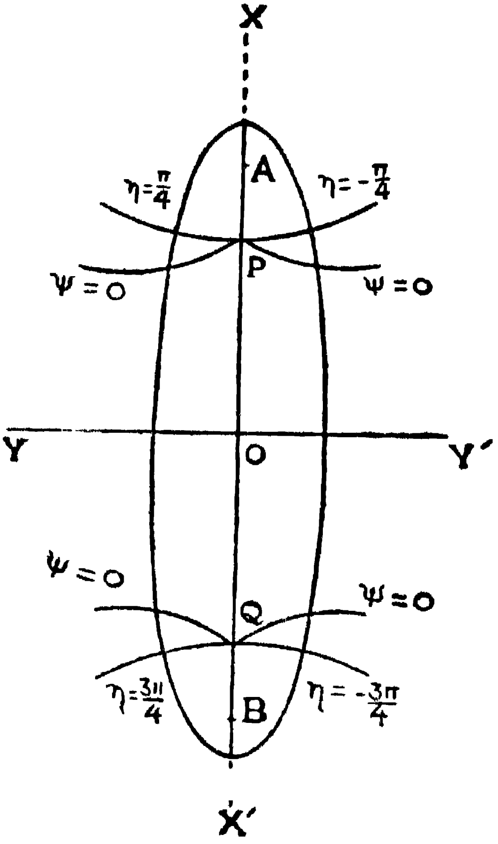

Fig. 7.

The stream line $\psi=0$, therefore, intersects the barrier at the points P and Q, where the hyperbolas $\eta=\pm\frac{\pi}{4}$ and $\eta=\pm\frac{3\pi}{4}$ intersect the line AB.

This result will only be slightly affected if we do not consider the current to strike the barrier at right angles, but at an angle slightly less than a right angle.

We will take a concrete case now.

The stream function is—

$$\frac{\psi}{c}=\sinh\xi\,(\mathrm{U}\sin\eta-\mathrm{V}\cos\eta)\;+\;\frac{1}{4}\,\omega' c e^{-2\xi}\cos 2\eta.$$

Let us take $\mathrm{V}=-30$ *m. p. h.*

$\mathrm{U}=\quad 5$ *m. p. h.*

We have $\omega'=0{\cdot}2\omega=3^\circ$ per hour

$c=400$ miles (about)

$\therefore\ \omega' c=400\times 0{\cdot}05$ *m. p. h.*

$=20$ *m. p. h.*

Therefore the stream function becomes

$$\frac{\psi}{c}=\sinh\xi\,(5\sin\eta+30\cos\eta)+5e^{-2\xi}\cos 2\eta.$$

We will now define the barrier $(x=\pm c)$ to be given by $\xi_0=0{\cdot}05$. Therefore $\sinh\xi_0=0{\cdot}05$, and $\cosh\xi_0=1{\cdot}00$. That is to say, the breadth of the barrier is 20 miles only, compared to its length of 800 miles. We get

$$e^{-2\xi_0}=0{\cdot}9.$$

The stream function therefore becomes

$$\frac{\psi}{c}=0{\cdot}05(5\sin\eta+30\cos\eta)+5\times 0{\cdot}9\cos 2\eta$$

$$=0{\cdot}25\sin\eta+1{\cdot}5\cos\eta+4{\cdot}5\cos 2\eta.$$

The stream function $\psi=0$ intersects the barrier $\xi_0=0{\cdot}05$ at the points given by

$$45\cos 2\eta+15\cos\eta+2{\cdot}5\sin\eta=0,$$

or,

$$90\cos^2\eta+15\cos\eta-45+2{\cdot}5\sin\eta=0.$$

Neglecting 2·5 sin η which is small compared with the other terms, we get

$$6\cos^2\eta+\cos\eta-3=0$$

or,

$$\cos\eta=\frac{-1\pm\sqrt{1+4\times3\times6}}{12}$$

$$=\cdot62 \text{ or } -0\cdot8$$

$$=\cos 51^\circ \text{ or } \cos\left(\frac{\pi}{2}+54^\circ\right).$$

$$\text{Therefore } \eta=\pm51^\circ, \text{ or, } \pm\left(\frac{\pi}{2}+54^\circ\right).$$

It is thus clear that the stream line $\psi=0$ will intersect any ellipse (ξ=const.) at four points.

To find out how rapidly the rotational term decreases with distance, we put $\xi=0\cdot5$, which gives sinh $\xi=0\cdot6$, cosh $\xi=1\cdot13$, $e^{-2\xi}=0\cdot36$. ξ thus represents an ellipse of which the major axis is about twice the minor axis.

We see that the value of ψ on this ellipse is given by

$$\frac{\psi}{c}=0\cdot6(5\sin\eta+30\cos\eta)+5\times0\cdot36\cos2\eta.$$

It will thus be clear that even at a distance represented by the ellipse $\xi=0\cdot5$, the term depending on the rotation has become negligibly small. The stream lines outside the ellipse $\xi=0\cdot5$ have very nearly the shape, as if rotation was absent. Within this ellipse, the rotation becomes more and more important as we approach the barrier, and the combined field due to the original current as well as the rotation determines the course of the stream lines. If the monsoon current is very strong, then it will preponderate over the relative motion introduced by rotation even within this ellipse except very close to the barrier.

It is obvious from the preceding discussion that the rotational factor becomes of importance simply because the mountains have large dimensions. Had the length of the

Western Ghats been only 100 miles instead of 800 miles, the rotational term would have been unimportant.

Obviously if the stream lines are drawn at closer intervals than what has been shown in Fig. 8 of the first paper, then there will be more than one stream line intersecting the Western Ghats. A diagram in which the theoretical stream lines have been drawn at closer intervals is given below (Fig. 8). As a result of the rotation, an asymmetry is introduced in the configuration of the stream lines round the barrier.

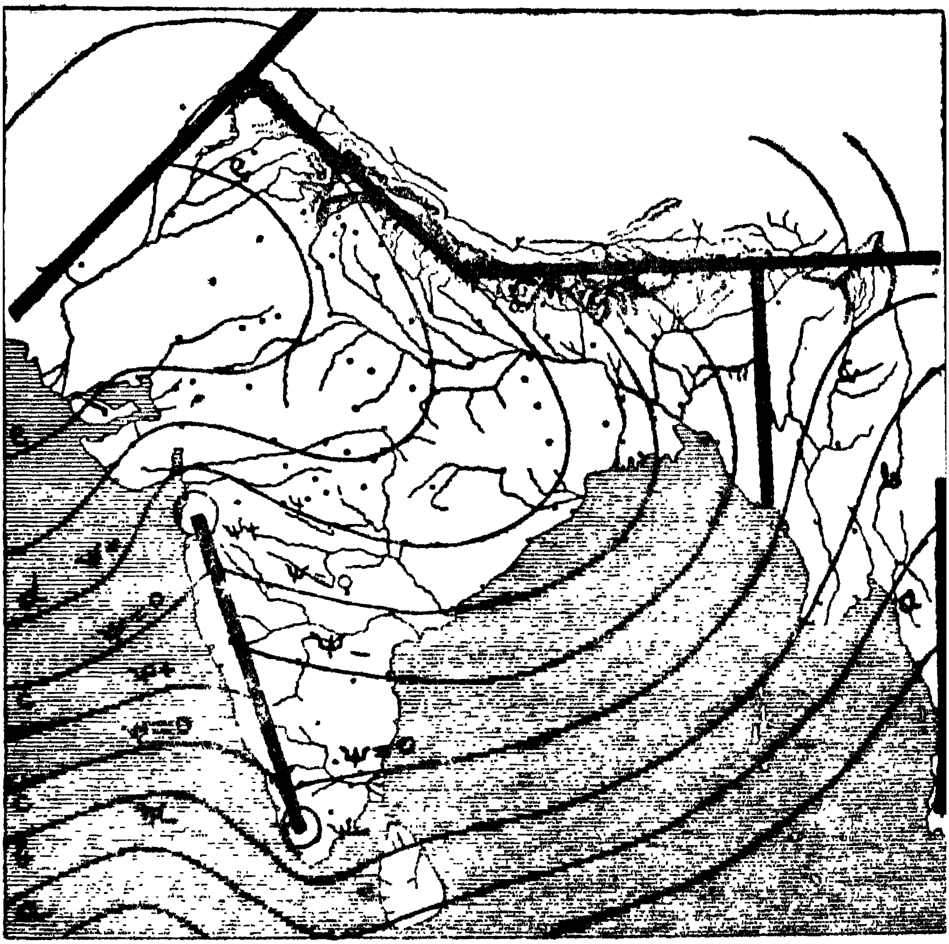

Fig. 8.

7. *Theoretical Stream Lines in the Average Monsoon Current over India.*

We shall now proceed to explain how the theoretical stream lines shown in Fig. 8 have been obtained. They represent the stream lines in free air, where the effect of the ground friction has become insensible, say, at 0·5 km. level, on the assumption of pure horizontal motion. The most important point to remember is, as already explained, that the thermodynamical factors and the hydrodynamical factors arising out of the rotation of the mountain barriers have combined to form a deep 'Low' in the neighbourhood of Sind necessitating the shifting of the centre of the 'Low' from Central Asia to that region. As a result of this shift of the centre of the 'Low' the expression

$$\psi = Vx - Uy$$

representing stream lines in Field No. 1 will no longer represent accurately the stream lines over India. This expression must now be replaced by

$$\psi = \log r,$$

where r will now measure any radius vector from the centre of lowest pressure over Sind. In other words, the stream lines in Field No. 1 will now be a series of circles having their centres in the centre of the lowest pressure area over Sind.

The stream lines are continuous and not discrete lines. In drawing the stream lines therefore one should not consider the different parts of the field as separate entities. The course of a stream line will be determined by the combined action of Field No. 1 and Field No. 2 as it travels from one part to the other part of the country.

The west-south-westerly current will first encounter the Western Ghats and the stream lines will undergo deformation as explained in the previous article. They will therefore take the shape in the neighbourhood of this barrier as shown in Figure 8 assuming that it is insurmountable. Stream lines such as '*d*' and '*c*' on arrival in the rear of the Ghats beyond its region of influence will come under the action of the corner formed by the mountain barriers over North-east India. It has already been pointed out that in the stream function due to this corner, the term $2Bxy$ is extremely important. This term will therefore exercise a powerful influence and make the stream lines take up hyperbolic shape with the Burma hills almost as asymptotes. The deepened 'Low' mentioned above will introduce the necessary curvature and the earth's rotation the direction of motion, so that the stream lines will enter the north Bay of Bengal from the south or south-westerly direction and take up the hyperbolic paths as soon as they come under the influence of the rectangular corner over Assam. But as the rotation of the barrier introduces the term $A\ (x^2-y^2)$ in the stream function, the stream lines will finally intersect the Himalayan Range as explained in the first paper. The approximate equation for determining the points of intersection of the stream lines with the Himalayan Range, as given in the first paper, will not be substantially modified even if we replace the current introduced by the 'Low,' namely,

$$\psi = Vx - Uy$$

by the more accurate form

$$\psi = V \log r,$$

where r denotes the radius vector from the centre of the 'Low' over Sind and V now merely represents a constant. For, taking the origin at the rectangular corner D (Fig. 1), the axis of x in the direction ED and the axis of y in the direction CD and the centre of the 'Low' at the point O on the x-axis, the co-ordinates of the centre will be $(-a, 0)$. Therefore the stream function is

$$\psi = V\ \log\left\{(x+a)^2+y^2\right\}^{\frac{1}{2}} + A(x^2-y^2) + 2\ Bxy.$$

The point of intersection with the x-axis will be given by

$$\psi = V \log (x+a) + Ax^2.$$

But a is very large compared with the abscissa of the points of intersection within the region under discussion. Therefore x/a is small.

We thus get $$A\,x^2 + V \log \left(1+\frac{x}{a}\right) - (\psi - V \log a) = 0.$$

But $$\log \left(1+\frac{x}{a}\right) = \frac{x}{a} + \frac{x^3}{3a^3} + \text{etc.}$$

We thus get approximately

$$x^2 + \frac{V}{Aa}\,x - \left(\frac{\psi}{A} - \frac{V \log a}{A}\right) = 0.$$

If we write $$\frac{V}{Aa} = V',$$

and $$\frac{\psi}{A} - \frac{V \log a}{A} = \psi',$$

we get $$x^2 + V'x - \psi' = 0,$$

determining the points of intersection. This is the same equation as given in the first paper.

Stream line, such as '*b*,' will after entering the Bay of Bengal assume a circular shape under the influence of the 'Low' over Sind, but will be outside the influence of the rectangular corner over Assam. It will therefore enter Burma, and assume hyperbolic shape under the influence of the rectangular corner over Burma formed by the east Himalayan Range and the Burma hills.

The stream line '*e*' being so near the deepened 'Low' over Sind will assume very nearly a circular shape, and for reasons explained in the first paper intersect the Frontier hills. If, as in the first paper, we take F (Fig. 1) as the origin of axes, GF as the positive direction of x-axis, and FE the positive direction of y-axis, and if further we assume the centre of the 'Low' to be at the point O, whose co-ordinates are $(-\beta, 0)$, then, the stream function ψ for north-west India is given by

$$\psi = \mathrm{V} \log \left\{ (x+\beta)^2 + y^2 \right\}^{\frac{1}{2}} + \mathrm{A}\ (x^2 - y^2) + 2\mathrm{B}xy.$$

The points of intersection with the x-axis, for which $x<\beta$, will therefore be given by

$$\mathrm{V} \log (x + \beta) + \mathrm{A}x^2 - \psi = 0,$$

or,

$$x^2 + \frac{\mathrm{V}}{\mathrm{A}} \log (x + \beta) - \frac{\psi}{\mathrm{A}} = 0,$$

or.

$$x^2 + \frac{\mathrm{V}}{\mathrm{A}} \log \left(1 + \frac{x}{\beta}\right) - \left(\frac{\psi}{\mathrm{A}} - \frac{\mathrm{V}}{\mathrm{A}} \log \beta\right) = 0.$$

Now

$$\log \left(1 + \frac{x}{\beta}\right) = \frac{x}{\beta} + \frac{x^3}{3\beta^3} + \text{etc.}$$

For finding an approximate value of the point of intersection, we can consider x/β to be small. We therefore get

$$x^2 + \frac{\mathrm{V}}{\mathrm{A}\beta}\, x - \left(\frac{\psi}{\mathrm{A}} - \frac{\mathrm{V}}{\mathrm{A}} \log \beta \right) = 0,$$

which determines the two points of intersection of the stream line with the barrier (x-axis). The stream lines thus form closed curves round the corner formed by the Himalyan Range and the Frontier hills.

Fig. 8 gives an instantaneous picture of stream lines. If a picture showing the paths of air particles were drawn, it would be quite different from this figure. On the assumption of pure horizontal motion, no path of air particles will intersect a barrier except at a point where there is 'dead air.' Under steady condition, the configuration of the instantaneous stream lines will continue to remain the same relative to the country and the barriers whenever the picture is drawn. The value of the 'constant' assigned to any particular stream line at the instant, $t=0$, will, however, continue to undergo a change with the march of time. It will in general be a periodic function of t. If the field under consideration be restricted to a limited region, say, the region round the Western Ghats, then the period will be of the order $2\pi A/\omega \sin \phi$, where A is a constant and ϕ the mean latitude of the region. The values assigned to some of the stream lines in Figure 8 are merely those given by the equations of art. 6. If *relative* values were assigned to these stream lines at another instant, they would be different from those given in the figure.

I have already explained that the synoptic sea-level isobars may be considered to represent approximately the instantaneous stream lines in the air at 0·5 km. level. We can therefore make a direct comparison of the isobars with the theoretical stream lines given in Fig. 8. A comparison of the normal isobars during the monsoon months, June to September, as given in the *Climatological Atlas of India* with the theoretical stream lines as drawn in this figure indeed suggests a very close agreement. The minor discrepancies between the observed and the theoretical stream lines are obviously due to the fact that the idealised mountain ranges differ widely from the actual mountain ranges. As shown in the first paper, the configuration of the theoretical stream lines explains why there is a trough of low pressure over the Gangetic plain. Undoubtedly the thermodynamical causes help the maintenance of this trough of low pressure.

The stream lines near the ground surface given by Bjerknes from the normal directions of wind in July (Fig. 3) indicate, as one should expect on theoretical grounds, that they generally intersect the normal isobars, and consequently, the theoretical stream lines in free air at angles which vary within certain limits (*vide* equation 10). The form of these stream lines is, however, somewhat complicated in view of the fact that they have been drawn irrespective of any consideration of the contour of the ground surface. They do, however, show, as already explained, (1) the equiangular spirals having their poles at the centre of the 'Low' over Sind, (2) the deformation produced by the southern portion of the Western Ghats where the height of the barrier is greatest, some of the peaks reaching an elevation of 7,000 to 8,000 feet, and (3) generally hyperbolic shape due to the corner over North-east India. It is also seen that at some distance away from the Himalayan Range, each stream line assumes a form as if it will strike the mountain. They do not however strike the Himalayan Range. For, as a general illustration of the principle embodied in the formula (1 2), each stream line on the surface on arriving at the *trough of low pressure* over the Gangetic plain tends to assume the shape of an equiangular spiral. This is clearly shown in the diagram. The northern half of the Ghats, where the elevation is generally low, is shown to produce very little deformation on these stream lines.

8. *Vertical Current.*

The preceding discussion has been based on the assumption of a pure horizontal current. This assumption is not true even approximately on an individual day during the monsoon months. There is condensation over many parts of the country and liberation of latent heat leading to the development of strong vertical currents. This effect will be more marked in the windward side of the barriers than in other places. It is therefore necessary to enquire how far in the motion which we obtain by averaging the data for many years, we eliminate the vertical current.

We cannot obtain a reply by a mere reference to the lapse rate. For, even if we assume the monsoon air to have a dry adiabatic lapse rate up to the condensation level, the monsoon current will be perfectly stable according to Richardson's criterion[1] of turbulence unless there is a vertical gradient of wind of a certain order. As Richardson has pointed out, near the ground surface up to a height of about 0·5 km., we can ordinarily expect the existence of such a vertical gradient of wind, but above that level such gradient will not always prevail. Besides, instability in the case of air in motion will merely mean the tendency to form turbulence. There will be innumerable eddies from a few feet to two or three hundred feet in diameter. These will have as much tendency to fall as to rise causing what we would picturesquely call 'atmospheric stirring.' In such cases, when the motion is averaged over the data for many years there will be no vertical motion.

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[1] Proc. Roy. Soc., Vol. 97, A (1920).

We can, however, see that if over any particular place there is vertical motion at all time from day to day and throughout the monsoon months, then averaging will not eliminate the vertical motion. As explained in the first paper we have two distinct factors, which will produce appreciable vertical motion, namely, (1) ground friction, and (2) thermodynamical causes.

The thermodynamical causes which develop a 'Low' must involve vertical motion. For this reason, averaging will not eliminate the vertical motion over the 'Low' in Sind. For the same reason, there must also be some vertical motion in the trough of low pressure over the Gangetic plain, which will not be eliminated by averaging. The fact that in Bjerknes' diagram the stream lines are seen to meet each other over this trough does suggest a vertical motion.

Owing to the complexity of the phenomenon involved under (2), it was completely ignored in the first paper, although this is by far the most important factor which contributes to the production of vertical motion. As shown in the first paper, during its travel over the ground surface, a vertical motion will be introduced in the monsoon current, the intensity of which will vary according to the nature of the surface. The monsoon current is so moist that even the very small upward vertical motion in the shape of turbulence produced during its travel over the roughened surface of the sea is sufficient to start condensation. This effect is much more pronounced over the rugged ground surface. The condensation will liberate a large amount of latent heat. The vertical motion which will be induced on account of the liberation of the thermal energy in this way will far outweigh that originally produced by surface friction. Assuming statistical laws to be approximately true, we can apply Exner's formula,[1] namely,

$$\frac{d^2z}{dt^2} = g \left[\frac{T_0}{T_0'} \left(1 - \frac{\alpha z}{T_0'} \right)^{\frac{\gamma}{\alpha} - 1} - 1 \right],$$

where $\frac{d^2z}{dt^2}$ denotes vertical acceleration, T_0, T_0' the initial temperatures of the rising mass of air and of the surrounding air, α the lapse rate of the surrounding air and γ the adiabatic lapse rate, to calculate the height to which a small air mass will rise as a result of this liberation of thermal energy. Indeed, Linke[2] has calculated by means of this formula several concrete cases for various assumed differences of temperatures of the mass and surrounding air and for various lapse rates. His calculations show that if the initial difference of temperatures is large then the height which an air mass can reach in this way may sometimes be considerable. The liberation of thermal energy must occur over isolated places and consequently the ascensional movements due to this cause must be localised phenomena. Over ordinary rough grounds an ascending current, in whatever manner it may be caused, must be counterbalanced by a descending current. On considering the average effect for many years, we would therefore get no vertical motion.

We are thus left with what will happen near a mountain barrier, and we therefore proceed to enquire whether the monsoon air near the sea level on impinging a mountain barrier will pass over it or move sideways. Obviously, if the current is capable of ascending over a mountain, the path of air particles will pass over it and not round it. If this process continues throughout or for an appreciable portion of the monsoon months, then averaging will not eliminate the strong vertical motion near the barrier, and the paths of the air particles even under the average condition will lie over the mountain and not round it. The most important case which requires consideration is that of the Western Ghats.

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[1] Dynamische Meteorology, 2nd Edition, p. 51.

[2] Met. zeit., p. 256 1928.

9. *Can the Sea-level Monsoon Air ascend the Western Ghats ?*

We shall proceed to discuss this question with the help of Figs. 9 and 10. In Fig. 9, the monsoon air is shown ascending the Ghats *en masse* in stream line motion. Let us assume that the mean velocity of the monsoon current between sea-level and the level of 4,000 feet is 25 miles per hour.

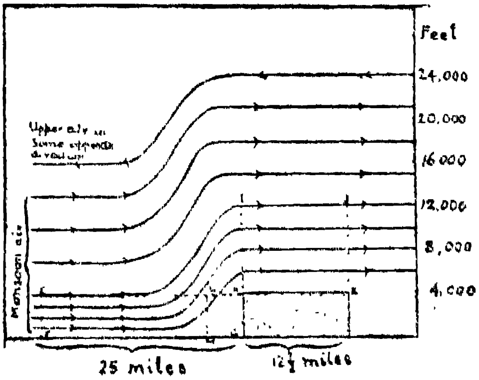
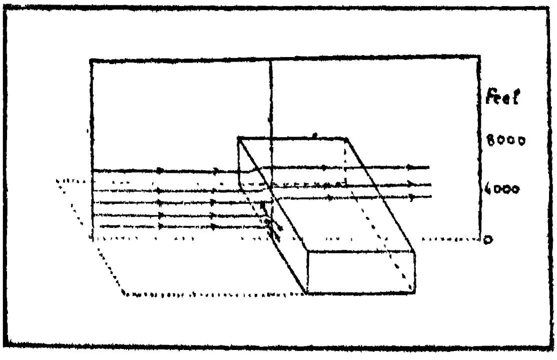


Fig. 9.



ig. 10.

This current must undergo a diminution in horizontal velocity on impinging the barrier. We assume that on the average the horizontal velocity of the current has decreased to half its original value when it has ascended over the mountain. We thus see that the volume of air included between EFGH will be lifted up to the position IHKJ every hour (Fig. 9). Since there is a decrease in density with height, we must have

volume IHKJ$>$volume EFGH.

Consequently the centre of gravity of the mass will be raised from a height of about 2,000 feet to a height greater than 8,000 feet. In performing this feat, the mass of air must do work at the expenditure of its "total energy." Let us now concentrate attention on a small volume LMGH (Fig. 9) very close to the barrier, and assume that the horizontal velocity of this volume has been almost completely destroyed by the barrier. Let us now apply the equation of energy to this volume. If T=kinetic energy, V=potential energy, W=internal energy of the mass of air LMGH, u, v, w the components of velocity, p the pressure and l, m, n the direction cosines of the normal to an element dS of the bounding surface, then the energy equation for this mass of air is

$$\frac{D}{Dt}(T+V+W)=\iint p(lu+mv+nw)\,dS.$$

Over the ground surface and also over the barrier,

$$lu+mv+nw=0.$$

Since the horizontal velocity has been almost completely destroyed, $lu+mv+nw=0$ over the face LM. Consequently in rising up the mass must do work against the superincumbent pressure. The work done in rising over the Ghats is, therefore, considerable and the energy must be derived from the decrease in T+V+W.

Let us now compare this motion with that shown in Fig. 10. In this case the air mass is shown to move sideways, and the diminution of the total energy involved in the motion, as shown in this figure, is a minute fraction of that in the previous case. It is a fundamental principle in dynamics (principle of least action) that a dynamical system will move with the minimum expenditure of energy. According to this principle the movement must necessarily be as shown in Fig. 10 and not as shown in Fig. 9.

We have already seen that in the month of May, the motion round the Western Ghats is in accordance with the principle shown in Fig. 10. During June to September, the stream lines as represented by the isobars pass over the northern part of the Ghats without much distortion, but undergo considerable bending round the southern part. The height of the northern part is small, between 2,000 to 4,000 feet, compared with the southern part, where it varies from 4,000 to 8,000 feet. An air mass can therefore get over the northern portion with a smaller expenditure of energy than over the southern.

The difference in the behaviour in the month of May and that in the other months is obviously due to the fact that in the month of May there is very little precipitation over and in the neighbourhood of the Ghats, while in the other months there is large precipitation. In the energy expression T and V are definite quantities and, when there is no precipitation, W is also definite, for then the internal energy can work only by adiabatic cooling. But when there is precipitation, W becomes complicated and indefinite, owing to liberation of latent heat, and the energy required for ascending over the Ghats is then fully obtainable from $T+V+W$.

If w_0 represents the initial vertical velocity, m the mass of air enclosed in the volume LMGH (Fig. 9), and if h be the height to which the c. g. of the mass will be raised before the vertical velocity is reduced to zero, then the energy equation becomes

$$\tfrac{1}{2}mw_0^2 - mgh = \left[\iiint p(lu+mv+nw)dS\,dt - W\right]_A^B,$$

where A and B denote the initial and final positions of the mass. We thus get

$$w_0^2 = 2gh - \frac{2}{m}\left[W - \iiint p(lu+mv+nw)dS\,dt\right]_A^B.$$

If

$$\left[W - \iiint p(lu+mv+nw)dS\,dt\right]_A^B = 0,$$

or, in other words, if the decrease in internal energy is equal to the work done against pressure, then the height reached will be very small and will be given by the usual formula[1] $w^2 = 2gh$. But, in general,

$$\left[W - \iiint p(lu+mv+nw)dS\,dt\right]_A^B$$

will not be equal to zero. When the ascent is accompanied by condensation, this expression will be fairly large. Consequently the height reached will be considerably more than that given by the formula $w_0^2 = 2gh$. An air mass can therefore have the required energy for ascending over the Ghats under special circumstances, particularly when the ascent is associated with precipitation.

When, therefore, the liberation of latent heat by condensation leads to strong vertical motion, the possibility of the current being driven over the mountain must be postulated. In his well-known paper, Pockels[2] has shown that an air

[1] The numerical figures given in art. 4 of the first paper are applicable only to this limiting case.

[2] "The theory of the formation of precipitation on mountain slopes," *vide*, "The Mechanics of the Earth's Atmosphere, Smithsonian Miscellaneous Collections." Third collection by Cleveland Abbe.

mass can ascend over a mountain having a gentle slope in the direction of the wind if accompanied by precipitation. But there are limitations in the practical application of Pockels' investigations. He considers the problem in two dimensions, namely, in a vertical section. The mountain is assumed to extend in the transverse directions to infinity. The air has not been allowed any exit in the transverse directions. His method is therefore equivalent to telling the air as follows:—"Here you are, I put you in hydrodynamical equations, which allow you to move in your own direction of motion or in the vertical direction. You will not be permitted to move sideways. Now you can choose which way you will move." Obviously under these limitations, the air must go up the profile. Similar limitations apply to the more recent investigations of Raethjan.[1] The investigations of these two authors do, however, demonstrate that it is possible for an air current to ascend a gentle slope under certain conditions. This however does not mean that the air will necessarily move up a slope, if there are other ways of exit which it can find with less expenditure of energy. Its motion in every case will be determined by the principle of least action. If, on any particular occasion, the air motion near the Ghats, along its entire length or any part approximates to the two-dimensional conditions investigated by Pockels, then the air will have no other way of exit except ascensional movements. Thus, for instance, if the monsoon current strikes the Ghats perpendicularly along its entire length or any appreciable part of its length, then it will obviously pass over the Ghats. Such a case may often arise when the current is highly unstable and there is intense precipitation on the windward side of the Ghats. Since, during the months June to September, there is intense precipitation in the windward side of the Ghats, it is clear that averaging will not entirely eliminate the vertical motion in this region.

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[1] Met. Zeit., pp. 292, 329, 383 and 420 (1929).

10. *Observed Air Motion in the neighbourhood of the Western Ghats.*

We have unfortunately very few observational data showing the manner in which air moves in the neighbourhood of the Ghats from day to day. On three different occasions I made some careful visual observations of the movements of low clouds from Khandala, a station on the Ghats, and found that they invariably moved round a peak but never over it. The observations are best made during occasional breaks in the rain when isolated clouds float about. The observer should stand in a convenient position and watch the movements of the clouds with reference to some definite point, such as a peak.

We can make some indirect calculations of the amount of air which ascends over the Ghats from the rainfall recorded at different stations over the Ghats. We assume as before that the Ghats have a uniform height of 4,000 feet. We assume also that the monsoon current has the average velocity of about 25 ft. per sec. (17 m.p.h.) and that it strikes the Ghats perpendicularly. It is clear that on meeting the barrier the horizontal velocity of the air stratum between the sea-level and the level of 4,000 feet will be completely destroyed. We would thus get a mass of almost saturated air, 4,000 feet thick, ascending steadily at the rate of 25 ft. per sec. This ascending air, 4,000 feet thick, should therefore produce at normal temperature rainfall at the rate of about 2·6 inches per hour or about 62 inches per day. On the average, we would therefore get at an observing station 7,613 inches[1] of rain during the four months June to

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[1] It will be seen from Fig. 9 that this ascending air mass must also cause the superincumbent air to rise at the same time. In the example, rainfall due to this cause has been neglected.

September. The average observed rainfall at a station over the Ghats probably does not exceed 400 inches or about 5 per cent. of the calculated rainfall. The calculated rainfall of 7,613 inches will probably occur over the windward edge of the summit along a narrow belt over which air will apparently be ascending at the full rate of 25 ft. per sec. and rapidly decrease on either side. So also will be the observed rainfall. This will not alter the percentage relationship between the observed and calculated rainfall. The figure of 400 inches taken for the observed rainfall is fairly high and comparable with that at Cherapunji (424 inches). Judging from the records of the few stations over the Ghats, it is probably an over-estimate. If so, the percentage relationship will be still lower. This result suggests that only a small fraction of the air mass ascends over the mountains and the rest moves sideways.

We found that, if on the assumption of pure horizontal motion we draw an instantaneous picture of the stream lines, for equidistant values of ψ, then a barrier can be intersected by more than one stream line. We explained that this result will merely mean that there will be either " dead air " close to the barrier or if there is no " dead air," the paths of the air particles, when time is taken into consideration, will pass round the barrier. We now see that the assumption of pure horizontal motion does not strictly hold close to the barrier. The air will be disposed of not only sideways but also vertically upwards. The analysis will therefore partially break down very close to the barrier, where, as pointed out in the first paper, the motion will be highly turbulent in character. Close to the barrier, therefore, we must draw the pictures of the stream lines both in the horizontal and vertical sections. The general character of the motion in the neighbourhood of the Western Ghats will, however, be obvious from the preceding discussion.

11. *Summary.*

A detailed analysis has been given of the various points which were briefly discussed in a previous paper, Ind. Journ. of Phy., Vol. IV, pp. 476-502. It is shown that on the rotating earth, a corner formed by two mountain ranges will have a tendency to develop closed stream lines in its neighbourhood. The corner formed by the Himalayan Range with the North-West Frontier Hills, therefore, helps the thermodynamical factors to fix up the position of the area of lowest pressure in the wide low pressure region extending from North-west India to North Africa during the monsoon months over Sind. If the corner did not help the development of closed stream lines, the area of lowest pressure instead of being over Sind could very well have been over the Sahara. To determine the influence of the mountain ranges on the air motion, two fields of stream lines are defined in the paper. Field No. 1 represents the stream lines which will be produced on the rotating earth by the thermodynamical mechanism, assuming that the mountain barriers were all absent. Field No. 2 represents the relative motion which will be produced in the air over the rotating earth by the mountain barriers alone, if the thermodynamical mechanism was absent. It is shown that the two fields are compoundable and when compounded they represent approximately the true stream lines in the air. On the assumption of pure horizontal motion, which is approximately true when the motion is obtained by averaging the data for many years, it is shown that during the monsoon months, the instantaneous field of stream lines over North-east India is expressible in the form

$$\dot{\psi} = Vx - Uy + A(x^2 - y^2) + 2Bxy,$$

where the constant B is considerably larger than the constant A. The stream lines over North-east India, therefore, assume hyperbolic shapes with the Burma hills almost as asymptotes.

They strike the Himalayan Range on account of the presence of the term $A(x^2 - y^2)$ in the stream function. A detailed analysis has been given of the deformation produced in the stream lines by the Western Ghats and full explanation has been given as to how the theoretical stream lines in the monsoon current can be drawn over India as a whole. The normal isobars give an instantaneous picture of the observed stream lines at 0·5 km. level and they are therefore comparable with the theoretical stream lines. It is shown that they agree closely with the theoretical stream lines. The *peculiarities* in the configuration of the normal monsoon isobars are thus shown to be due to a very large extent to the mountain ranges. Bjerknes' diagram of stream lines drawn from the observed normal directions of wind in July is shown to present features agreeing approximately with the theoretical stream lines near the ground surface.

A discussion has been given of the air motion very close to the barrier where the assumption of pure horizontal motion, even under the average conditions, does not hold good.

I hope to revert to the subject for further development at the earliest opportunity.

THE OBSERVATORY, BOMBAY.
Oct. 22, 1930.

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A Study of the Raman Effect in Certain Substances with a New Apparatus.

PROF. B. VENKATESACHAR AND L. SIBAIYA.

(Plates XXVII and XXVIII)

ABSTRACT.

An apparatus for the study of the Raman effect in which the exciting arc is produced in the annular space between two coaxial tubes, the inside one being of fused silica and the outside one of pyrex glass, is described. The substance under examination is placed in the inner quartz tube and is surrounded on all sides by the exciting arc. In this arrangement strong ultra-violet lines such as the resonance line of mercury (2536Å) may be used as the exciting radiation. The temperature of the substance can be varied by sending a current of air through the inner tube; the effect of change of temperature on Raman lines has been thus examined. Calcite and aragonite have been studied with this new apparatus. Halite and fluorite give negative results. Acetylene gas gives Raman lines corresponding to the infra-red absorption bands at 2.45 μ and 7.5 μ; the latter comes up as a double line corresponding to the points of maximum absorption recorded by Levin and Meyer. The strong absorption band at 13·7 μ gives no corresponding Raman line. The temperature effect on the continuous wings accompanying unmodified lines in the scattered spectrum has been studied and their origin suggested.

The original method of Raman[1] which consists in concentrating the exciting radiation on the scattering material by means of a lens and that of Wood[2] in which a long mercury arc is placed parallel to the tube containing the substance, a liquid usually, are now well known. Wood has used another method [1]: he surrounds the tube having the substance under examination by a spiral discharge tube containing helium. Recently in the case of solids Menzies [2] and others use the substance in the form of powder.

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[1] Ind. J. Phys., Vol. 2, p. 387 (1928).

[2] Nature, Vol. 123, p. 166, Feb. 2 (1929).

The arrangement of apparatus described below is the result of an attempt to secure the following ends in the study of the Raman effect.

(*i*) The method must be applicable to solids (including powders), vapours and gases.

(*ii*) The temperature of the scattering material must be capable of being varied and under control.

(*iii*) It must be possible to use as the exciting radiation such strong lines in the ultraviolet as 2536Å of mercury.

The present apparatus has been designed with the idea of surrounding a quartz tube containing the scattering material by a long column arc discharge in mercury. The inside tube, S, (Plate XXVII) is of clear fused silica passing centrally through an outer pyrex tube, T. The tubes are joined together by two iron caps with shellac or DeKhotinsky's cement. The main arc runs between the double tungsten anode A_2 and the mercury cathode K. In order to facilitate the starting of this long column arc, provision is made for a subsidiary arc between A_1 and K. Bulbs B_1 and B_2 are intended to prevent the glass from melting by coming too near the hot anodes. The region of discharge between the inner and outer tubes is kept constantly pumped out by a Hy-vac pump. The following is the procedure adopted in starting the arc:—When the vacuum is sufficiently low the mercury in K is heated till it

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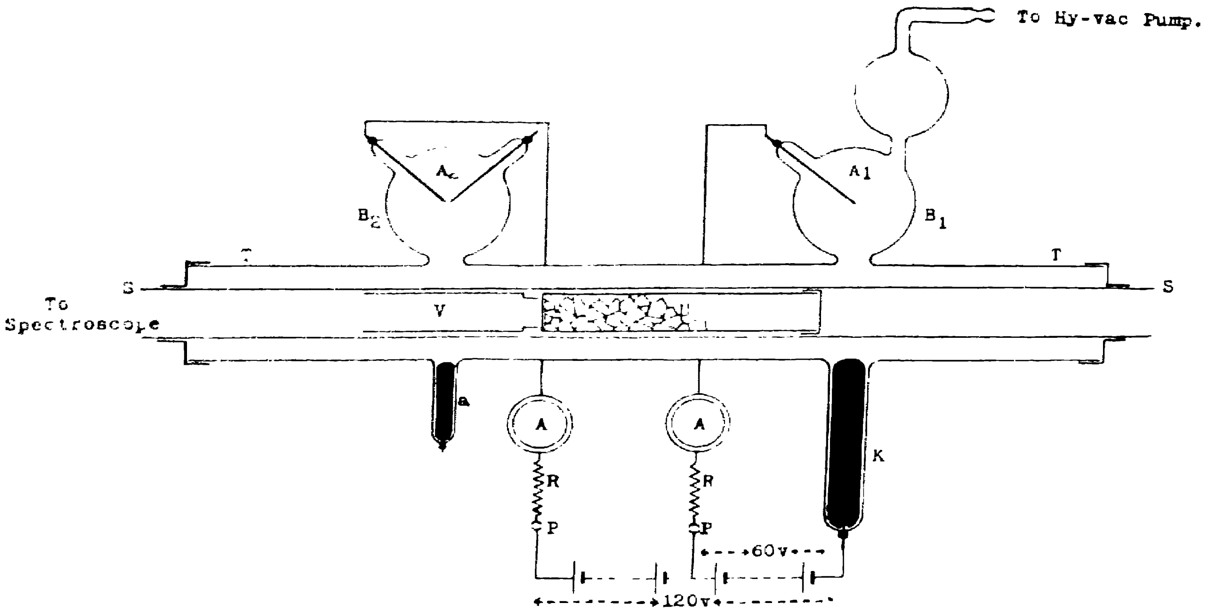
[1] Phys. Rev., Vol. 33, p. 294 (1929).

[2] Menzies, Nature, Oct. 5 1929).
Bär, Nature, Nov. 2 (1929).
Krishnamurti, Nature, Mar. 22 (1930.)



An apparatus for the study of the Raman Effect.

A—ammeter. A_1 A_2—anodes a—subsidiary anodes. B_1 B_2—Pyrex glass bulbs. SS—Inner Quartz tube. K—cathode. TT—outer Pyrex tube. RR—rheostats U—Quartz tube containing the scattering material. PP—switches. V—iron tube.

boils and an induction coil discharge is passed between it and an additional anode, a, provided for the purpose ; the arc between K and A_1 now lights up and carries a current of about 5 amperes. Next the portion between B_1 and B_2 is well heated and on again passing the induction coil discharge the main arc between K and A_2 is established. After this arc has run for about five minutes the subsidiary arc may be put out. On the completion of an experiment, when it is desired to switch off the main arc, the current must be gradually reduced and the outer pyrex tube slightly warmed and annealed after putting out the arc. This will invariably ensure a longer life on the average for the pyrex tube, which otherwise by sudden cooling is liable to crack.

The diameter and thickness of the annular space determine whether the arc completely surrounds the inner quartz tube or not. In our experiments when the arc completely surrounded the inner tube the diameters of the tubes were 2 and 3 cms. In other cases, especially when the diameter of the inner tube was increased, the arc nearly but not completely surrounded the quartz tube. Various distances between B_1 and B_2 ranging from 15 cms. to 50 cms. have been tried : but when this distance is very much diminished the arc takes a spiral form.

The main arc runs steadily for hours without much attention and usually the shellac at the iron caps, when sufficiently far from the region of discharge, does not soften. But when it is desired to cool the scattering material by a stream of air from an electric blower, the iron cap at the end where the air warmed by passing over the hot arc escapes, is cooled by a blast of air, say, from an electric fan or a hair-dryer. By the proper control of the supply of air for cooling the scattering material the temperature can be altered by more than 200°C and the material can be maintained at any desired temperature within five degrees. The range of available temperature is from about 120°C to 400°C. The current in the main arc is usually ten amperes with a potential drop of 50-60 volts between the terminals; the current density in the arc is about two amperes per square centimetre.

Raman effect in solids.—The substance is placed in the form of powder (crystalline or amorphous) in a fused silica tube, U, with a silica plate fused on to one end, the other end being closed by a loosely fitting iron cap. An iron tube, V, is placed on the spectrometer side against the silica plate to allow only the scattered light from the substance in the central portion of the tube to fall on the spectrometer. A quartz lens is used to concentrate the light on the slit.

Raman effect in vapours and gases.—A fused silica tube (Fig. 1) with a graded seal ending in pyrex glass is used.

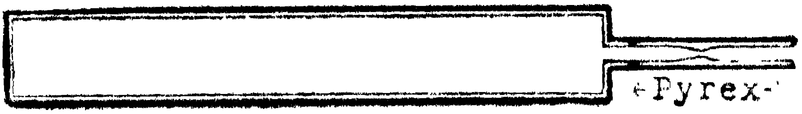


FIG. 1.

The amount of scattering material whether it be a gas or a vapour should be so regulated before sealing off the tube as to develop a pressure not exceeding ten atmospheres at the temperature of the arc. In the case of vapours, after the introduction of the required quantity of the liquid, the tube is evacuated to remove air and sealed off.

With the view of testing the effectiveness of the method calcite was tried at two different temperatures. It was placed in the tube, U, in the form of small crystals. The following table embodies the results obtained:

TABLE I

Exciting Line.		Raman Lines.			dν Obs. cm⁻¹.	λRaman in μ.	λ in μ values of other observers.	
λ in Å.	ν vac.	λ in Å.	Int.	ν vac.				
2536·52	39412	2545·8	2	39269	143	70·4	68	Vide Plate xxviii
		2527·5	1	39552	140			
		2549·0	1	39219	193	51·5	...	
		2524·0	0·5	39607	195			
		2551.1	2	39141	271	36·6	25·8	
		2519·0	1	39686	274			
		2583·2	1	38700	712	14·05	14·08	
		2608·4	4	38326	1086	9·25	9·23	
		2468·7	1	40195	1083			
		2632·1	1	37981	1431	6·98	6·96	
3125·66	31983	3235·5	2	30898	1085	9·25	9·23	
3131·56	31923	3242·2	2	30834	1089			

While these results are in substantial agreement with those obtained by other investigators([1, 2, 3, 4]), there are also the following new features. The highly intense resonance line of mercury 2536Å gives a sharp Stokes line of great intensity corresponding to the inactive frequency 1086 cm⁻¹ of the CO_3-radical. The anti-Stokes line for this frequency comes out clearly on the plate. The intensities of anti-Stokes lines in the case of the low frequencies 142 and 273 cm⁻¹ are comparable with those of the corresponding Stokes lines whereas in the case of the inactive frequency the anti-Stokes line is very feeble. It is interesting to note that the infra-red absorption band at 11·4μ gives no corresponding Raman line.[5] This band, according to Nielsen,[6] arises on

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[1] Krishnan, Ind. J. Phys., IV, p. 131, Aug. (1929).

[2] Wood, Phil. Mag., Vol. 6, 729 (1928).

[3] Kimura and Uchida, Inst. Phys. Chem. Research, Tokyo Sc. Papers, 203, pp. 199-204 (1929). Jap. J. Phys., 5, p. 97 (1928).

[4] Nisi, Proc. Imp. Acad., Tokyo, 5, p. 127 (1929).

[5] Kimura and Uchida, Inst. Phys. Chem. Research, 203. (1929).

[6] Phys. Rev., Vol. 32, pp. 773-778 (1928).

account of the vibration of the carbon atom along the axis of symmetry in the CO_3 radical.

Effect of temperature.—The Raman line corresponding to the inactive frequency is not perceptibly affected in sharpness when the temperature is increased from 150°C to 250°C. But all the other Raman lines become distinctly more diffuse with rise of temperature. The anti-Stokes lines are enhanced in relative intensity as the temperature increases. Raman has directed attention to this effect in the following words; "As the temperature is increased, since the proportion of molecules in a higher energy level also increases, we should expect the negative lines to brighten up relatively to the corresponding positive lines."[1]

Our results with aragonite, though in general agreement with those of others,[2] show that the Raman line corresponding to the inactive frequency is relatively far fainter than in calcite (Plate XXVIII). It is not however clear whether the presence of this Raman line is due to traces of calcite invariably found mixed up with aragonite or to the slow paramorphous conversion of aragonite into calcite at our working temperatures.[3] Chalk powder gave a negative result.

Landsberg and Mandelstam,[4] Nisi and others working with fluorite (CaF_2) have invariably obtained a negative result. Under the favourable conditions of our experimental arrangement, we have tried fluorite and halite (NaCl). Even the strong line 2536Å of mercury gave no trace of Raman lines after long exposures amounting to 40 hours. In the case of fluorite, however, the usual fluorescence spectrum came out on the plate with marked intensity extending from 5000Å to 2900Å with an intensity maximum at about 3400Å.

Raman Effect in Acetylene.—The infra-red absorption

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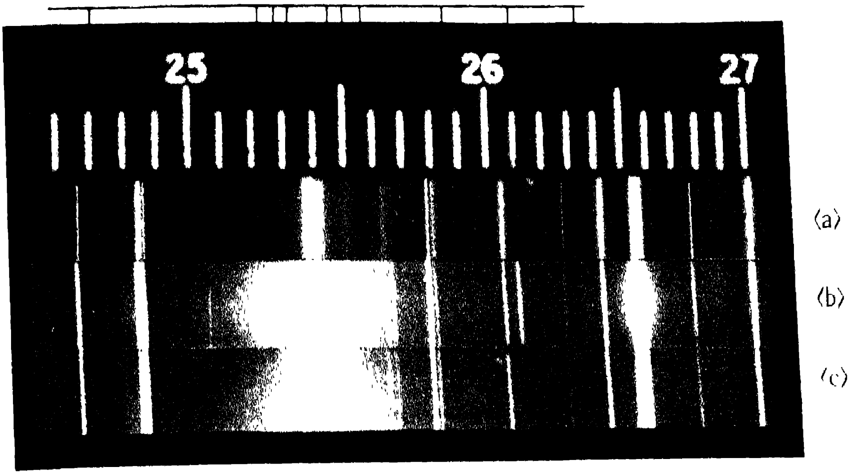
[1] Proc. Roy. Soc., Vol. 122, p. 29 (1929).

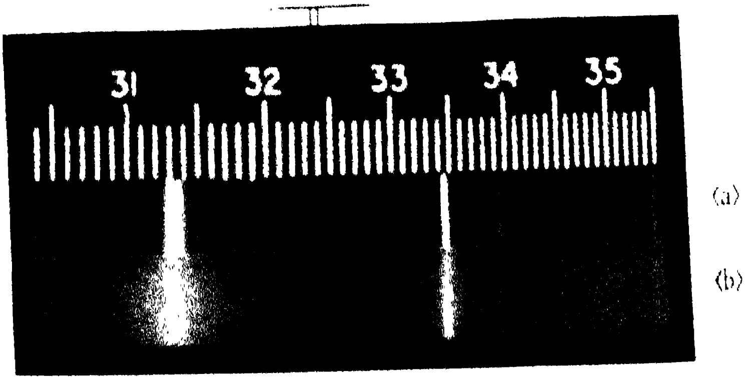
[2] Kimura and Uchida, Tokyo Sci. Papers, p. 203 (1929).

[3] Bulletin 770; The Data of Geochemistry, pp. 557-558 (1924).

[4] Zs. f. Phys., 50, p. 769 (1928).



(a) Incident spectrum
(b) Raman spectrum of Calcite
(c) Raman spectrum of Aragonite



(a) Incident spectrum
(b) Raman spectrum of Calcite.

spectrum of acetylene has been studied by Coblentz[1] who finds absorption maxima at 13·7μ, 7·5μ and 2·5μ. We examined spectroscopically the radiation scattered by a column of about 40 cms. of acetylene contained in a long pyrex tube at a pressure of 2·5 atmospheres. This pyrex tube occupied the place of the central silica tube, S, thus limiting our observations to the visible region. The following table contains the results obtained :—

TABLE II

Exciting Line.		Raman Line.			Observed $d\nu$ cm^{-1}	λ Raman in μ	Infra-red values of λ in μ.
λ (Å).	ν vac.	λ (Å).	Int.	ν vac.			
4046·6	24705	4845·7	1	20631	4074	2·45	2·5
4077·8	24516	4889·3	1	20447	4069	2·45	2·5
4046·6	24705	4269·2	0·5	23418	1287	7·76	7·5
4046·6	24705	4294·8	1	23277	1428	7·00	
4077·8	24516	4300·7	0·5	23245	1271	7·86	7·5
4077.8	24516	4325·4	0·5 diff.	23113	1403	7·12	

We see that there is no Raman line corresponding to the strong infra-red absorption band at 13·7μ. There have been instances of strong infra-red absorption bands of which the corresponding Raman lines do not appear. Pringsheim and Rosen[2] have listed several such cases. This however, does not rule out the possibility of the faint appearance of the Raman line for 13.7μ on longer exposure than we have been able to give. The wave-number shifts of the Raman lines for 7·5 μ seem to correspond to the points of maximum absorption of this band as recorded by Levin and Meyer.[3]

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[1] Carnegie Inst. Pub., 35 (1905).

[2] Zs. f. Phys., 50, XI, p. 741 (1928).

[3] J. O. S. A., Vol. 16, Mar. (1928).

One of the features that comes out markedly on the plates (Plate XXVIII) is the hazy wing extending on either side of strong exciting lines in the scattered spectrum. This phenomenon has been observed by several investigators[1] and its origin is even now a matter for speculation. On our plates these wings are seen not only in the case of substances like calcite which show the ordinary Raman effect but also in substances like halite and fluorite which do not exhibit the effect. We find that the temperature of the scattering substance influences the wings in that an increase of temperature relatively enhances the effect on the violet side (anti-Stokes side) of the incident line with the result that the wing develops a decided assymmetry about the unmodified line when as in the case of calcite the temperature of the substance is raised from 150°C to 250°C. The wings may be traced to about 25 Å on the violet side and to about 15 Å on the red side of the incident line 2536 Å in calcite at 250°C. This behaviour of the wings with change of temperature suggests that the phenomenon has to be traced to the interaction of the thermal energy of the molecules, considered for instance as Planck's oscillators, with the incident quantum.

We take this opportunity of thanking the Geology Department of this College for kindly lending us aragonite, fluorite and halite used in this investigation.

DEPARTMENT OF PHYSICS,
CENTRAL COLLEGE, BANGALORE.
Dated 5th November, 1930.

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[1] Daure, C. R., 186, p. 1583 (1928). Raman and Krishnan, Proc. Roy. Soc., 122, p. 23, (1929). Faraday Society Discussion on Molecular Spectra, Cabannes, p. 808 (1929).

Atmospheric Electric Potential Gradient at Bangalore.

By

PROF. A. VENKAT RAO TELANG.

(Plate XXIX)

1. *Introduction.*

The determination of the Electric data of the atmosphere has passed into the ordinary routine of the most important observatories in Europe and other parts of the civilised world. In India, a consistent and continuous series of observations has not been made. G. C. Simpson published the results of observations at Simla covering a period December 1908—May 1910.[1] Only relative values are given, as it was not found feasible to obtain the factor of reduction to level. No other station appears to have taken up this work systematically since.[2] One of the difficulties which seems to have discouraged some observers is the difficulty of preserving insulation, especially during the extremely humid months of the South-West Monsoon. It was therefore thought desirable to obtain results continuously over a fairly long period at Bangalore.

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[1] Memoirs of the Indian Meteorological Department, Vol. XXI, Pt. VI.

[2] Recently observations have been started at the Colaba Observatory, Bombay.

2. *Situation and Climatic Data.*

Bangalore is in Latitude 12°58′ N and Longitude 77°36′ E at a height of 3,000 feet above mean sea level. The standard time adopted for observation is 5½ hours Greenwich time. The accompanying tables show the seasonal and climatic conditions.

The seasonal conditions may be described as below.

In January the N.E. monsoon prevails with occasional showers and fairly strong and steady winds. February and March are dry with little rain or cloudiness, showing, however, thin cirrus clouds at a high level on many days, generally towards noon and later. There is a tendency to dustiness and haze. April and May are hot summer months often alleviated by thunderstorms towards the end of the day. There is generally little steady wind except when there is a storm. With June the South-West monsoon with strong winds and cloudiness establishes itself. In the earlier part there is little rain, leading to dustiness. Later rains and drizzles occur. This state continues into July and August. In September the wind moderates and rain is more frequent. In fact September is the rainiest month of the year. In October there is a pause of the South-West monsoon before the North-East one begins. The wind is only slight and there is moderate rain. This continues into the earlier part of November. The North-East monsoon begins in November and continues through December into January. These are the cold months.

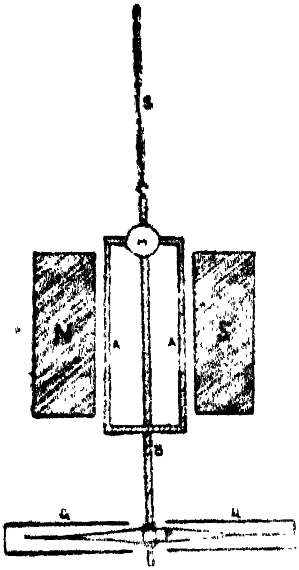
Months.	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Mean.
Rainfall average of 1917-26.	·46″	·11″	·41″	1·59″	4·68″	2·71″	2·98″	4·66″	6·92″	3·95″	2·60	·45″	$\frac{31·85}{12}$
Cloudiness % at 8 A.M.	32	19	11	28	45	76	86	87	80	62	52	39	51
Wind Vel. daily miles.	133	125	129	110	129	192	192	170	129	102	113	126	136
Temperature ...	58·2°F.	60·7	65·1	69·5	69·3	67·1	66·2	65·9	65·7	65·3	62·3	58·6	64·5

Seasonal data for Bangalore.

3. *Apparatus.*

The instrument for recording the potential gradient is a quadrant electrometer, rendered dead-beat by an electromagnetic device (Fig. 1). The reflection of a vertical

Fig. 1.

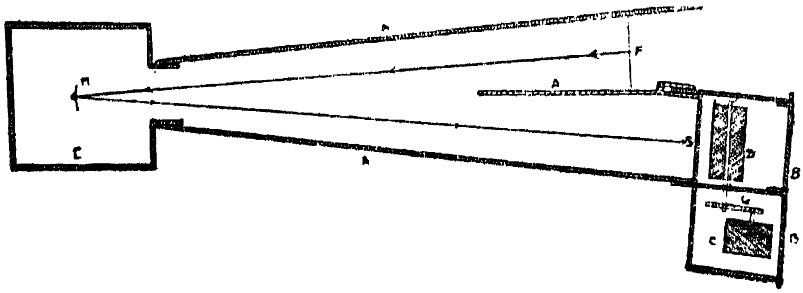


Dead-beat arrangement for Electrometer.

S,—Phosphor bronze suspension of electrometer needle. B—Spindle carrying the needle P. A, Aluminium rectangle fixed to the spindle whose rotation between poles N, S of permanent horse-shoe magnet causes the instrument to be dead-beat. M—Concave mirror. Q. Q—Quadrants.

incandescent filament falls on a fine horizontal slit in the recording camera, and so a spot of light travels about horizontally on a photographic paper wound on a drum inside the camera-box. This drum is rotated about a horizontal axis parallel to the slit by clockwork, so as to turn round once in one day or two days as required (Fig. 2). The collector

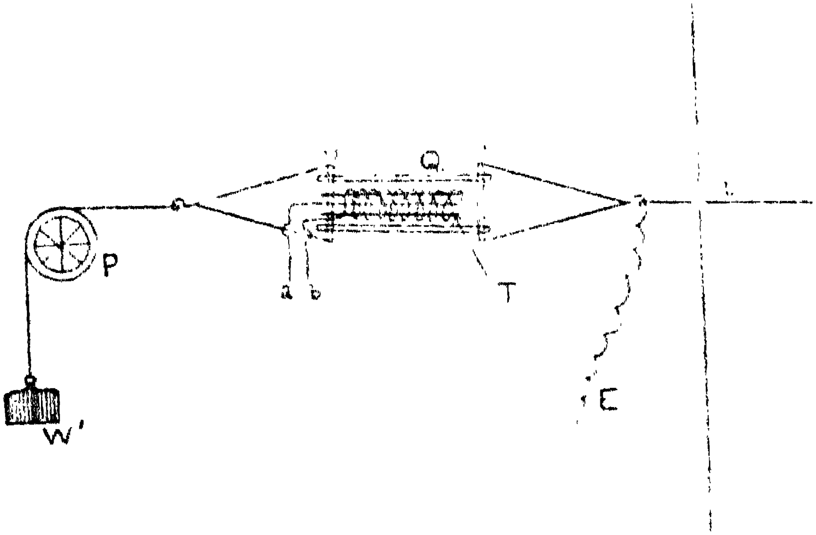
Fig. 2.



Recording Camera.

E—Electrometer, M—the concave mirror. A. A. is a box through which rays from a vertical glowing filament F pass, are reflected by M, and form an image just be hind S, a horizontal slit in the front of a box, B_1B_2 having two compartments, B_1 in which is mounted the drum D on horizontal spindle and B_2 in which is the clock C driving the drum by means of gear wheels G.

Fig. 3.

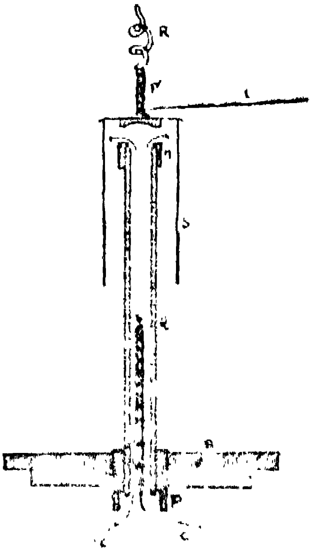


Insulating Shackle to keep line under tension.

Q is a tube of quartz inside which is introduced a glass tube, T, with a heating coil wound on it (terminals a, b). Q is grooved slightly about one centimeter from each end and a stout copper wire W is fixed on each groove. From W stretch loops of thinner wire keeping clear of the ends of the quartz tube. To the loop on one side is fixed the line L and on the other side a string passing over a pulley and carrying a weight W; this keeps the line L tight and level in spite of any elongation which may occur. The line passes on without tension to the electrometer.

is a spiral coated with a radium salt, and mounted on an insulating support at some particular position at some distance from the walls of the building (Fig. 4). A line, *i.e.* a copper wire, runs from the collector to an insulated shackle inside the room to keep it under tension and thence to the needle of the electrometer (Fig. 3).

Fig. 4.



Insulating Support for Collector.

B is the block carrying the pulg P. which supports a quartz tube Q vertically. C-C. heating coil terminals. M metal cap on top of Q which carries S- a thin copper sleeve shielding the upper part of Q from the weather and P′ a pin which supports the collector R and the line wire L.

4. *Insulation.*

The insulation at the different parts, *viz.*, the electrometer head, the shackle, and the support of the collector, was specially attended to. Vulcanite was used, and was found fairly satisfactory with special devices for protection. As however this insulation was liable to break down during rain and to a certain extent in very moist weather, this method of insulation was given up in favour of quartz tube insulators kept warm, *i.e.*, maintained constantly some degrees above atmospheric temperature. The warming was carried out in one of two ways, *viz.*, a heating coil was kept within the quartz tube, or a concentric glass tube not touching the quartz was kept hot by means of an electric current through a coil wound on it (the glass tube). In the second case the quartz was kept warm by radiated heat. (Figs. 3 & 4.)

The heating current was from an 8-volt alternating current source, the conveying line being earthed at one point. The insulation obtained by these means is excellent in all kinds of weather, except for a short time in very heavy rain, as verified by frequent tests. In fact, daily tests were found quite unnecessary.

5. *Zero Changes and Calibration.*

One of the quadrants of the electrometer is earthed and the other connected to the positive terminal of a battery of cadmium cells of which the negative terminal is earthed. The sensitiveness of the instrument could be altered by varying the number of cells used. Two cells were ordinarily used. An automatic device was employed to disconnect the second quadrant from the positive terminal of the battery and earth it exactly at each hour for about two minutes. This marks the hours and gives the zero line on the record. It also helps to test the adjustment of the instrument continuously.[1]

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[1] NOTE.—Before the above device was employed a different arrangement was tried, *i.e.*, to earth the line with the electrometer needle at the end of each hour. The present method is superior in that it gives automatic correction for want of exact adjustment of the instrument; thus:

If the instrument is slightly out of adjustment, the deflection $\delta = a.V + b\,V^2$ where V is the needle voltage, large in comparison with the quadrant potential to which 'a' is proportional while 'b' is independent of it. If now with the same volts on the needle, both the quadrants are earthed 'a' becomes zero and the present deflection $\delta' = bV^2$. Hence $\delta - \delta' = aV$. This means that on measuring the ordinate $\delta - \delta'$ we get a quantity proportional to V, whence V can be calculated, since 'a' is constant and easily determined.

The calibration of the record for volts, *i.e.*, the determination of 'a' is carried out by charging the needle to some known voltage for about two minutes at the beginning and end of each record.

6. *Co-efficient of Reduction to Level.*

To obtain from the potential recorded by the instrument the potential gradient on the level, simultaneous observations were made with the recording instrument and a portable instrument. This latter was an instrument of the gold leaf type suitably calibrated. A collector similar to the one employed for records was mounted at a height of about four feet on a level plain near by and the potential measured with the abovementioned instrument. The co-efficient was found to be ·795.

7. *Results.*

From the records of each month were selected those for ten days on which there was no negative potential, nor any markedly violent oscillations of potential. It is difficult to find ten such days in certain months, usually in the period March-August, when either due to monsoon winds, thunder storms or dry dusty days, violent oscillations and frequent negative potentials prevail.[1] In such cases we have to be satisfied with a smaller number of days. If, in any month, the number of selected days available be less than five, no mean results are worked out for that month.

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[1] See Figs. 3, 4 in Plate.

TABLE I.

1927

Hour of day.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	Mean.
January ...	26·6	16·3	12·6	11·7	9·3	6·8	8·7	7·3	23·0	25·5	28·5	27·2	31·2	37·9	33·6	31·1	29·1	31·6	40·4	56·7	57·8	50·3	42·7	36·7	28·4
February ...	25·5	21·7	11·9	11·7	11·9	9·1	12·3	11·3	14·0	8·7	21·7	26·4	28·4	27·3	25·6	24·7	23·8	25·2	31·8	50·7	52·9	40·1	31·6	28·4	23·9
March ...																									
April ...	40·0	40·8	33·7	32·6	28·6	29·0	31·2	31·5	40·3	48·7	42·2	33·4	33·9	32·1	28·0	26·3	26·1	23·3	31·2	43·2	53·5	45·5	45·0	42·0	36·0
May ...																									
June ...																									
July ...																									
August ...	14·5	13·4	9·9	8·6	6·2	6·9	5·3	4·5	6·2	13·3	26·6	35·5	43·6	43·6	44·3	46·1	41·2	39·6	49·1	66·1	62·2	47·7	43·8	26·0	29·3
September ...	30·4	23·6	14·9	10·5	10·4	10·0	8·5	10·0	18·2	35·8	45·4	42·9	47·6	50·8	44·3	44·3	45·5	51·6	54·6	62·9	53·8	38·7	31·5	28·7	34·0
October ...	52·1	45·0	35·1	31·4	30·5	25·4	36·1	40·5	39·6	51·9	55·7	51·6	59·1	54·5	49·1	46·4	46·5	47·3	68·2	90·0	87·1	81·1	66·7	63·4	52·3
November ...	38·3	32·1	28·1	21·0	15·4	14·4	21·3	33·9	42·8	52·3	53·5	54·4	52·3	49·4	42·6	39·4	40·4	43·7	58·0	86·6	87·1	71·6	49·3	32·0	44·1
December ...	35·6	20·8	17·6	17·2	19·7	17·1	18·6	29·1	34·8	45·6	50·5	47·0	50·3	44·3	46·3	44·1	41·8	44·1	60·5	79·3	83·2	71·6	57·7	44·4	42·5

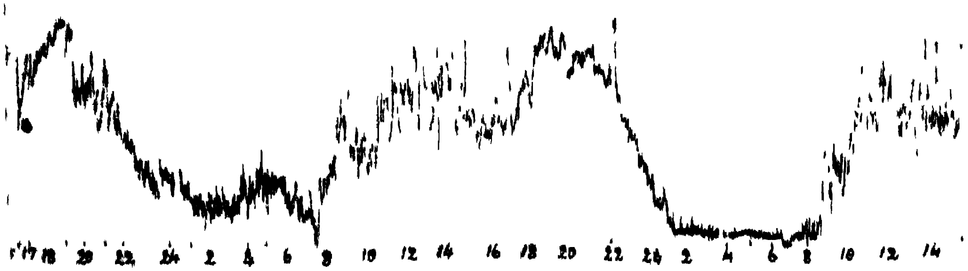
Monthly mean values of the potential gradient (volts/meter) at the different hours of the day——on fine days only

TABLE 2.

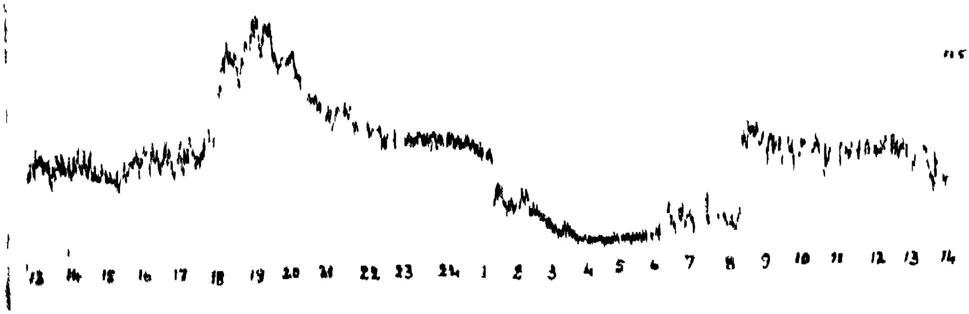
1928.

Hour of Day.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	Mean.
January ...	31·3	18·5	18·0	10·7	11·7	10·2	7·6	9·9	15·5	40·6	44·2	41·3	38·5	50·2	41·2	38·6	41·8	44·7	52·3	75·2	75·2	64·9	50·2	37·0	36·3
February ...	41·2	37·5	97·5	31·6	28·7	28·2	28·5	38·0	40·5	31·8	39·6	38·3	39·8	41·8	39·6	33·9	35·5	42·8	51·0	74·9	91·3	79·5	59·5	46·1	44·2
March ...	56·4	64·2	54·1	48·7	47·5	36·5	37·3	54·8	50·5	60·1	47·9	49·9	45·1	42·7	34·5	28·8	29·6	31·2	37·8	60·6	69·3	59·7	60·8	58·8	48·6
April ...	40·9	39·7	33·1	35·1	40·9	41·9	37·2	47·6	53·0	59·4	56·7	48·3	43·2	45·1	43·9	34·1	34·2	34·9	38·2	48·5	51·6	54·7	49·7	46·5	44·1
May ...	42·1	39·6	34·1	25·3	27·2	23·0	17·1	20·9	40·3	52·1	62·6	64·3	55·7	57·6	47·7	43·5	39·6	41·2	45·4	54·8	69·8	69·4	54·5	46·7	44·7
June ...	37·3	25·7	20·8	13·4	9·2	10·1	21·0	25·2	26·0	44·7	45·8	65·4	65·8	59·2	53·5	51·1	50·2	52·1	60·2	66·3	62·9	55·8	51·2	48·7	42·5
July ...	21·6	15·3	13·7	9·8	8·3	6·4	6·8	7·5	10·0	19·7	28·0	47·0	61·2	53·8	70·1	60·2	57·6	60·9	62·1	61·6	69·8	56·2	44·4	29·3	36·7
August ...	30·0	24·5	20·9	20·5	14·5	12·0	8·6	8·2	8·9	13·4	18·8	31·4	53·4	56·6	69·3	72·0	63·3	65·4	65·7	80·9	57·4	43·8	40·7	34·7	38·2
September ...	41·8	35·3	27·6	26·8	27·1	26·1	28·5	26·8	23·9	46·4	41·6	55·7	59·8	57·7	58·7	59·4	52·3	56·3	57·6	72·6	73·1	71·8	56·7	50·4	47·2
October ...	42·3	30·4	25·2	23·1	23·1	21·2	23·5	32·1	31·6	55·3	60·0	55·9	57·4	59·8	46·3	48·7	51·3	51·6	70·7	82·7	88·9	64·0	59·0	47·8	48·0
November ...	36·7	32·0	24·7	22·0	20·2	20·8	24·6	11·3	39·9	44·3	57·0	56·0	54·6	52·2	45·6	42·9	39·2	44·9	55·3	64·4	70·4	60·2	54·2	43·5	43·7
December ...	22·0	17·5	10·6	11·3	12·1	10·4	12·8	18·1	24·2	30·1	32·0	40·0	48·9	44·4	45·9	45·2	41·7	45·2	54·7	71·3	63·8	57·1	43·3	27·2	34·6
Mean. ...	37·0	31·7	26·7	23·2	22·4	20·6	21·2	27·5	30·4	41·7	44·5	49·5	52·0	51·8	49·7	46·6	44·7	47·6	54·2	67·8	70·3	61·5	52·0	43·0	42·4

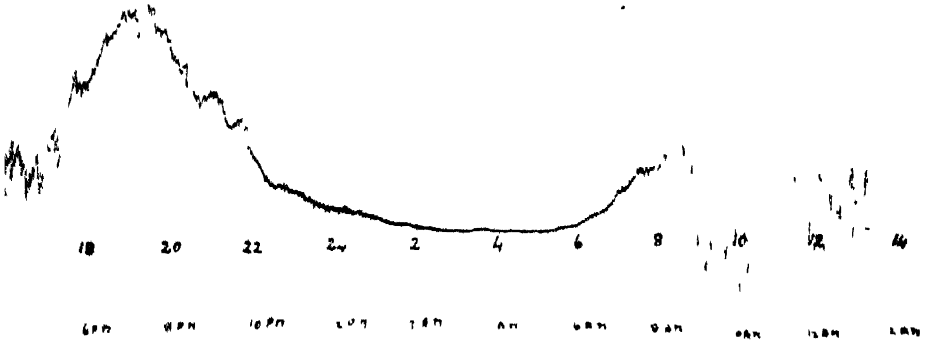
Monthly mean values of the Potential gradient $\frac{\text{volts}}{\text{meter}}$ at the different hours of the day—on fine days only.



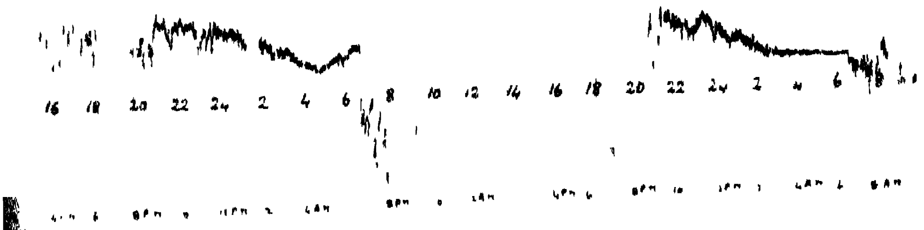
From 2nd Oct.1927, 16 Hrs. to 4th Oct. 1927, 16 hrs.



From 11th Jan. 1928,13 hrs. to 12th Jan. 1928, 14 hrs.



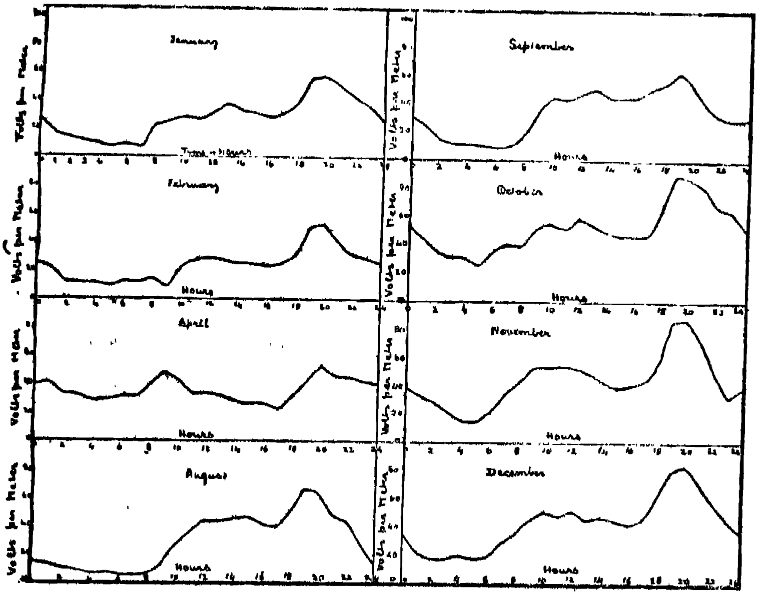
From 27th Oct. 1925,16 hrs. to 28th Oct. 1925, 14 hrs.



From 9th June 1926, 13 hrs. to 11th June 1926, 10 hrs.

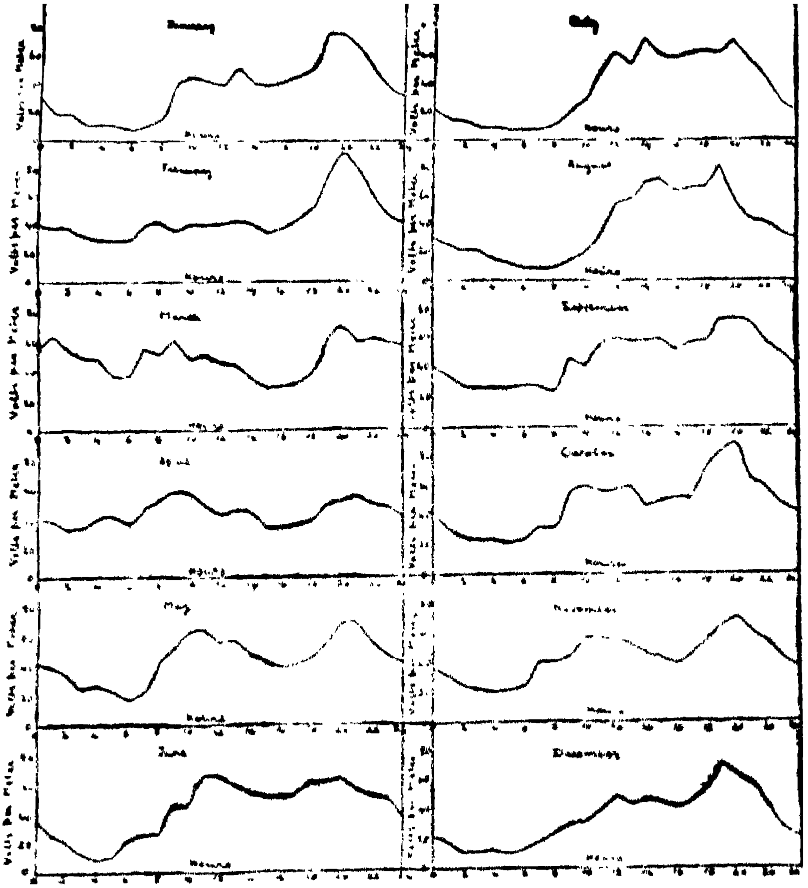
The hourly values of the potential on the selected days are determined (Tables 1 and 2) and the curves of mean diurnal variation drawn for each month, and the year. These curves are given in Figs. 5, 6 & 7. It will be seen that there are ordinarily two maxima and two minima each day. Of the minima the one near sunrise is the more important and lies between 5 and 6 hours. The other minimum is not so low and occurs between 15 and 16 hours. Of the maxima, the one in the evening is the outstanding one and lies between 19 and 20 hours. The other maximum in the earlier part of the day is neither always pronounced nor regular. It may occur anywhere between 8 and 13 hours. An examination of the accompanying graphs render it probable that there are really more maxima than one in this interval of time, of these some one maximum being prominent on any particular day. This produces the effect of a maximum whose time of occurrence

Fig. 5.



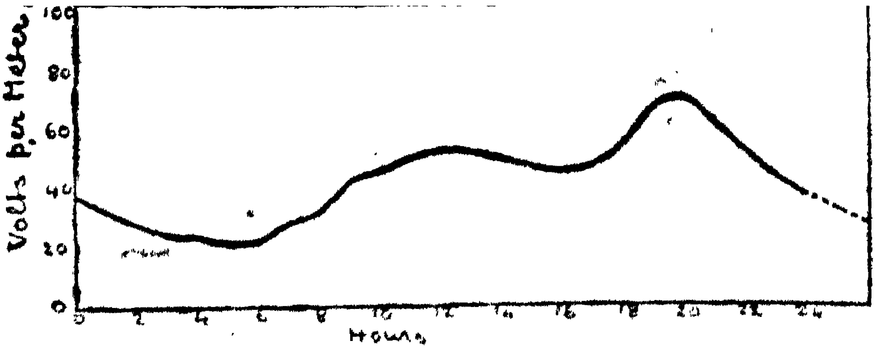
Hourly mean values of Potential Gradient on fine days for different months of 1927.

Fig. 6.



Hourly mean values of Potential Gradient on fine days for different months of 1928.

Fig. 7.

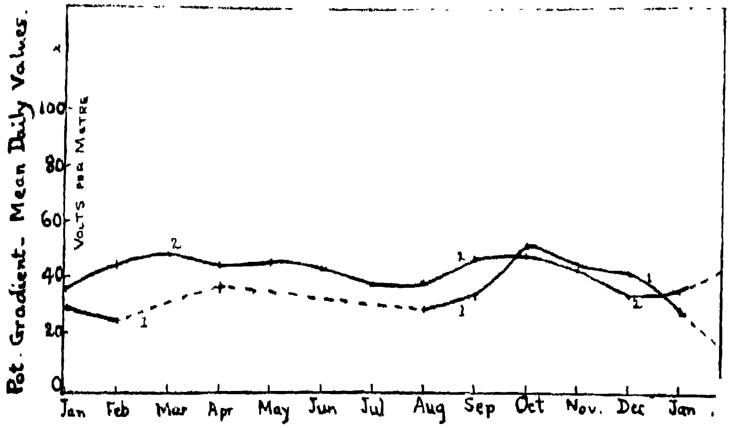


Hourly mean values of Potential Gradient on fine days for the whole year 1928.

is uncertain. On this basis we may notice maxima at the following times :—

8h, 10h, 12h, 13-14h. A method of dealing with this subject will be discussed in a different place. The changes in the diurnal curve with the months can be easily followed. In December and January the potential falls very low in the second half of the night and again in July and August. In the succeeding months there is a gradial change and in April the two minima and maxima are of nearly the same level, and the difference between a maximum and a minimum is least. Other particulars can be easily seen from the curves. The mean daily values change from month to month as shown in table and Fig. 8. The mean potential passes through minima in December-January and in July-August, and through maxima in March and in October.

Fig. 8.



Monthly mean values of Potential Gradient.

Curve 1 ... ... 1927.
Curve 2 ... ... 1928.

Department of Physics,
Central College, Bangalore.

6th November, 1930.